EMERGING TECHNOLOGIES IN DRINKING WATER

VENICE, ITALY

May, 1988

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AWWA RESEARCH FOUNDATION

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IN

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AWWA Research Foundation

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Acknowledgement and Disclaimer

All of the materials incorporated in this compendium were assembled by the American Water Works Association Research Foundation for a Workshop on Emerging Technologies held in May 1988.

PREFACE

The American Water Works Association Research Foundation organized a workshop on Emerging Technologies which was held in Venice, Italy in May 1988. The participating countries submitted their information to the AWWA Research Foundation who prepared and distributed this workbook to the participants prior to the meeting.

The Ontario Ministry of the Environment participated in the Venice meeting and collected the Canadian material. The Ministry, with the approval of the Research Foundation, is reprinting this material for distribution to the Canadian contributors.

EMERGING TECHNOLOGIES WORKBOOK

INTRODUCTION

PROJECT BACKGROUND

The objective of this project is to identify emerging technologies--innovative developments of all kinds--in the water supply field with two purposes in mind: (1) the collection and exchange of information among the participating parties and (2) the discovery of promising approaches that merit further research. In addition, the project may lead to cooperative ventures and continued information exchange among the participants.

This 1988 effort was the third phase of the Emerging Technologies Project. The first phase was conducted in 1984 and culminated in a meeting in Amsterdam, Holland. The second phase was conducted in 1986 with a meeting in Oxford, England.

Although funded by the American Water Works Association Research Foundation (AWWARF), the project depends upon the generous assistance of the correspondents in the various countries who gathered the information and upon those who prepared the actual project reports. Their names are provided in the "Attendees List" which follows this Introduction.

AWWARF wrote to potential participants in the Summer of 1987, requesting their cooperation. Project reports were solicited, written and collected during the remainder of the year. This workbook was prepared and distributed by AWWARF in early 1988, prior to a meeting of the participants in Venice, Italy, May 4-5, 1988. Additional materials submitted during the meeting have been added to this volume, along with the necessary revisions in the Table of Contents.

HOW THE WORKBOOK IS ORGANIZED

Project reports and papers are grouped by country. The countries are listed alphabetically.

Within each country, the reports and/or papers are given a reference number, called the AWWARF Code number. It is printed in the upper right-hand corner of the first page of each report. The reference code consists of the country's initials and a number.

The pages in each country section are also numbered for easy reference, with the country's initials preceding the page number (for example, FR-10 means page 10 of the French Section).

Please note that there is a Table of Contents following this Introduction. It lists the title of each report, its reference code number and its page number.

GENERAL CATEGORIZATION OF PROJECTS

The pages following the Table of Contents display the individual titles of the reports and papers submitted by each country, grouped into eleven general research areas. Please note that the United States Section includes an update of selected AWWARF activities.

It is important to note that this body of information is a representative sample of the research being conducted by the participating countries, not an all-inclusive collection.

NOTE OF THANKS

AWWARF extends its sincere thanks to the participants in this project. Without the aid of correspondents in other countries, this workbook and the project itself would not have been possible.

Very special gratitude is due our Italian hosts, FEDERGASACQUA, represented by Mr. F. Meucci, Director of the Rome Water Department. His zealous attention to detail in making arrangements for the Emerging Technologies meeting exemplifies the best traditions of Italian hospitality and ensured everyone an enjoyable meeting. The Venice Water Department ASPIV also provided generous, gracious support of our meeting and its Director, Mr. A. Rosa also merits our heartfelt thanks.

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AWWA RESEARCH FOUNDATION
REPORT FOR EMERGING TECHNOLOGIES PARTICIPANTS

JUNE 1988

The Foundation's centralized research program for the water supply industry of North America is a reality. The cooperative effort, which is being coordinated through the three organizations representing water utilities in the U.S. and canada -- American Water Works Association, the National Association of Water Companies, and the Association of Metropolitan Water Agencies --is helping the water utilities meet the challenge of the future and solve the problems of today.

Participation in the program was strengthened during the last twelve month period, resulting in an unprecedented income of over 3.4 million (projected) for 1988, and it appears that even this optimistic project will be surpassed. Water utilities are finding that participation is not only a responsibility to the industry but also that it can provide a beneficial return far exceeding their limited investment.

Research Program

Such tremendous strides were taken in the funding of research during the past year that it is difficult to put it into perspective. For instance, the amount of projects funded during the past twelve months came to $5.5 million which nearly equals the expenditures of the previous five years combined. The 30 projects activated since June of 1987, compared to an average of 17 per year in the past, attest to the fact that it was a banner period for the Foundation. The following generic statistics characterize the Foundation's research agenda:

- The implementation of the '87/'88 research agenda increased the percentage of funding devoted to "hard" research from 89 percent during the period from 1983 to 1987 to a level of 92 percent for the period through June 1988.

- Conversely, the technology transfer portion of the agenda decreased from 11 percent last year to 8 percent this year even though approximately $402,000 worth of projects were added in the last added in the last twelve months.

- Funding for unsolicited proposals--five of which were funded this past year--maintained a level of 15 percent of available research money; over $550,000 has been reserved for funding original research ideas in June of 1988.

- Research directed at water treatment processes continued to dominate the Foundation's agenda in '87/'88--16 new projects were approved in June and January which, when combined with previous projects, amounts to 44 percent of the funding available and 40 percent of the number of projects for the total six year period from 1983.

- Even though six new distribution system projects were added in the last year, the percentage devoted to this category slipped from 17 percent to 13.6 percent of the available funding over the entire period.

- Likewise, the monitoring/analysis research funding category dropped from 14 percent to 11.6 percent, despite the fact that five new projects, totalling more than one-half million dollars, were started in the last year.

- On the other hand, the percentage of the Foundation's research budget devoted to general regulatory issues confronting the water industry increased by one percent to 50 percent of the six year available funding--on 1987/88 there were 21 projects and over $2.7 million categorized as regulatory research oriented.

- Finally, a new health effects research category was added to the Foundation's agenda in the 1987/88 period with $535,00 amounted to 9.7 percent of the '87/'88 research budget and 4.8 percent of the budget during the six year period of review.

From 1983 through June 1988, the Foundation funded more than 100 research projects. Final reports have been published on more than a fourth of them; another fifteen are expected to be released in 1988. This steadily growing catalog of research reports and practical handbooks offers members and subscribers a diverse assortment of technical reference. Most water utilities will find that at least some of their problems and concerns have been addressed by the Foundation's program and that they will benefit from the findings.

Technology Transfer

The Board of Trustees elevated the Foundation's technology transfer function with the appointment of a Trustee committee to oversee the design and implementation of an optimum program. In the long term, this effort is seen to be critically important in the retention and recruitment of participants in the Research Subscription Program -- potential and existing members must realize and implement the practical value of the benefits of a centralized research program.
The Foundation has employed the following means of effectively transferring the technology from the research arena to the operational workplace:

- The Foundation's first video report on research, produced in 1987, describes five projects dealing with Giardia lamblia. During the first months of its availability, there were more than 1500 showings of the rent-free videotape.

- The Video on the Research Foundation's programs and activities entitled, "The Water Supply Challenge - A Cooperative Effort" has received rave reviews from the 300+ viewers that have seen it since its release in January 1988.

- The Foundation has staged four workshops in Philadelphia, Orlando, Universal City and Chicago during the first part of 1988 which attracted more than 375 attendees; 84 percent of the attendees rated it excellent or good and more than two-thirds said the information they received helped them solve an operational problem.

- More than 250 water industry personnel attended a workshop on research results co-sponsored by AWWARF and the US Environmental Protection Agency.

- Subscribers received copies of the executive summaries of each completed research project. Copies of the final reports are available on request to all subscribers at no charge.

- AWWARF's three periodicals, Water Research Quarterly, Research News, and Executive Report on Research, kept subscribers informed of research developments and Foundation activities.

- The Foundation's first "poster session"--reporting on 30 research projects--was presented at the 1987 AWWA Annual Conference. A similar program is planned for 1988.

- Through technology exchange programs with foreign institutions, the Foundation has been able to bring millions of dollars worth of its research to subscribers at little or no cost.

- AWWARF's fourth international Symposium on water reuse attracted more than 300 professionals to Denver in August, 1987. In a related matter it was decided to discontinue the Water Reuse News publication because of the general lack of interest.

- During the past 11 months, 5652 of the Foundation's 30 publications have been purchased; these publications are marketed and distributed through AWWA.

Over the past year, the Foundation has extended and improved its cooperation with other organizations. The primary purpose of

this has been to establish contacts within the research community, avoid duplicative effort, develop collaborative programs, and enhance the recognition and credibility of, the Foundation. The Foundation has had a long-standing relationship with EPA and the water research organizations in Holland, Germany, France, and England. The Gas Research Institute, Electric Power Research Institute, American Gas Association, American Public Works Association, and WPCF are cooperating in the production of the infrastructure workshop. The Foundation's sponsorship of the Emerging Technology workshop series and its participation in IWSA has enhanced the Foundation's international reputation.

Subscription Program

1988 began with almost 250 subscribing utilities providing nearly $3,000,000 to the research program. Another 100 utilities pledged to subscribe this year. By the end of the year, AWWARF hopes to have more than 400 Utility subscriptions worth more than $4,000,000. In addition, the Foundation has about 4000 dues-paying members, all industry organizations and companies, paying about $400,000 annually. The following graph shows the actual and projected income for '87 and '88.

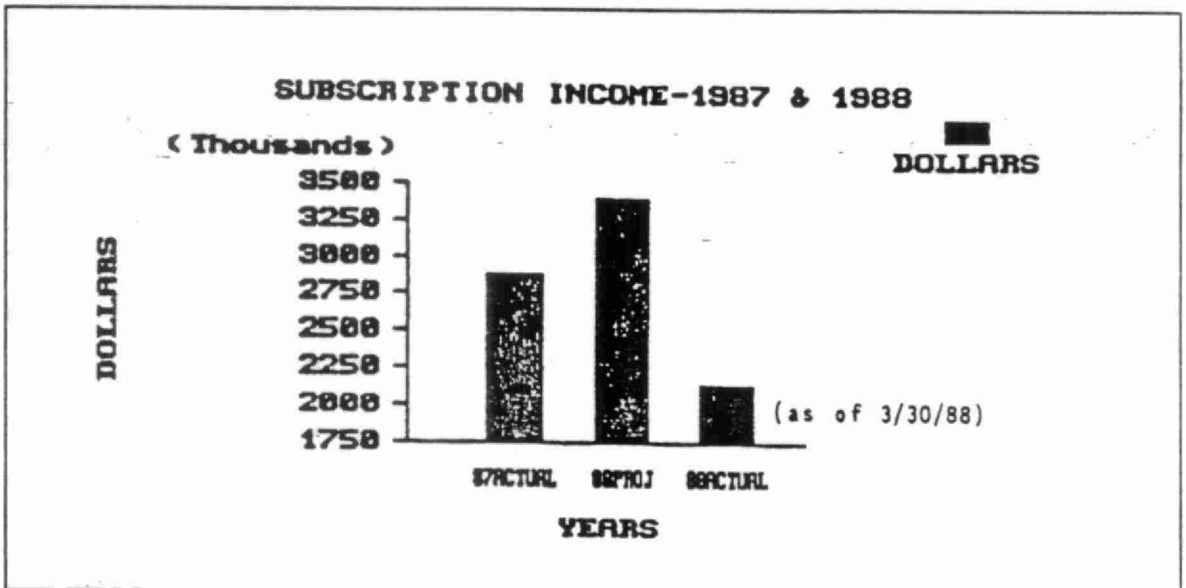

Figure 1

Doubling the research program in one year as was done in the last twelve months, doubles the potential return for every utility subscriber, with no increase in the individual utility's annual payment. Cooperative research pays dividends!

Since last June, the Foundation has finalized both its Five Year Research Plan and Corporate Plan. The research plan defines the Foundation's research direction and emphasis on a five year planning horizon. The Corporate Plan attempts to project the business development of the organization. Both plans will be revised in 1990.

Summary

During the past twelve months the Research Foundation has advanced along all major programmatic fronts--Subscriptions have increased, technology transfer activities have been enhanced, research projects have improved in both scope and number, and membership services have escalated. The past year brought an unprecedented amount of growth in terms of income to the Research Foundation and the organization responded in a very positive manner. The Foundation demonstrated conclusively that operational systems are in place to efficiently implement a major research program.

TABLE OF CONTENTS

TABLE OF CONTENTS

CANADA

SCANDINAVIA (NORWAY)

(SWEDEN)

SOUTH AFRICA

SPAIN

SWITZERLAND

TABLE OF CONTENTS (By Subject)

CONTROL AND REMOVAL OF ORGANICS

AUSTRALIA

CANADA

FRANCE

JAPAN

CANADA

FRANCE

ITALY

JAPAN

SCANDINAVIA (NORWAY)

SOUTH AFRICA

COAGULATION/FLOCCULATION/SEDIMENTATION/FILTRATION

CORROSION/DISTRIBUTION SYSTEM OPERATION AND MAINTENANCE

RADIONUCLIDES

SELECTED TREATMENT PROBLEMS AND OTHER RESEARCH ACTIVITIES

WATER PLANT OPTIMIZATION STUDY

AUSTRALIA

AUSTRALIA

EMERGING WATER SUPPLY TECHNOLOGY

AWWARF Code #: AU-01

PROJECT DESCRIPTION

Please send reports to:

Mr. John B. Mannion
AWWA Research Foundation
6666 West Quincy Avenue
Denver, CO 80235

Project Title:

REMOVAL OF NATURAL ORGANIC MATERIAL BY BIOLOGICAL PROCESSES ENHANCED BY PRE-OZONATION

Contact (name of person, organization, address, telephone):

MR DON BURSILL
AUSTRALIAN CENTRE FOR WATER TREATMENT AND WATER QUALITY RESEARCH
PRIVATE MAIL BAG
SALISBURY SOUTH AUSTRALIA 5108

TEL: (08) 259 0236

Project Description (Please attach a schematic diagram if appropriate):

This project aims to identify mechanisms for reducing high levels of natural organics prior to subsequent water treatment processes. Preliminary results indicate significant reductions can be achieved by pre-ozonation and microbiological activity.

The project work plan is attached.

Operating and cost data (including data on efficiency, results, etc.):

The estimated cost of the project is A$90,000 (staff and materials)

Place(s) of installation/application (including dates):

Laboratory based studies conducted at two of the Centre's facilities (i.e. Bolivar and The Levels). Pilot Plant facilities located at Hope Valley. (All locations are suburbs of Adelaide, South Australia).

Project Timetable October 1987 - December 1989

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

Internal Funding

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

AUSTRALIAN CENTRE FOR WATER TREATMENT AND WATER QUALITY RESEARCH

PROJECT: REMOVAL OF NATURAL ORGANIC MATERIAL BY BIOLOGICAL PROCESSES ENHANCED BY PREOZONATION

AIM

To develop strategies to reduce organics by biological processes in order to improve the quality of the water and the economy and efficiency of subsequent water treatment processes.

RESEARCH PLAN AND METHODOLOGY

1. Determination of the optimum conditions (flow rate, pH, temperature, etc.) for ozone generation, ozone absorption and maximum equilibrium residual ozone concentration in high purity water.

2. Determination of the rate of ozone decomposition in high purity water to subsequently enable calculation of the amount of ozone reacted with water contaminants.

3. Development of a reliable and appropriate method for the determination of the biodegradable fraction of dissolved organic carbon (BDOC) by determination of the optimum experimental conditions (pH, temperature, biomass used, etc.) for maximum dissolved organic carbon (DOC) removal. Water samples will be treated with ozone and stored for a set time. Innoculation of the water sample can be made either with a natural range of bacteria from the same origin as the sample, or with pure cultures of heterotrophic micro-organisms.

   The DOC concentration will be monitored constantly over the period set.

   Microbiological tests will be performed to follow the progress of bacteriological processes and identify the most effective species for the removal of DOC.

4. Determine optimum ozone doses for different waters at the optimum conditions for production of biodegradable organic carbon (as determined in 3). The effect of multistep ozonation as opposed to a large single dose will also be investigated.

5. Confirm that optimum ozone dose as determined in laboratory tests gives comparable results in pilot activated carbon filters. Assess type and depth of biomass in filters (could provide insight into better filter design).

6. Development of a rapid method of assessment of media to support biological growth using micro-organisms as determined in 3 and small filter assembly.

7. Optimum experimental conditions for DOC removal will be applied to long term storage system. At this stage it is envisaged that four tanks (above ground swimming pools, each approximately 13 m^3) will be used to simulate reservoir conditions.

8. Assess biological filter using optimum medium and same conditions as 7. This will enable assessment of need for a support structure.

   For 7 & 8, use changes in water quality (e.g. UV absorbance, colour, etc.) as well as subsequent water treatment processes (e.g. alum requirements, THM FP, chlorine demand, etc.).

9. Do mutagenicity tests on water prior and after biological treatment. Report these tests after alum treatment and chlorination to determine if removing precursors likely to form mutagenic products.

10. Assess alternative methods of increasing the biodegradable dissolved organic carbon (e.g. ultra violet irradiation).

11. On the basis of the above results, develop a large scale process which can be tried, firstly on pilot plant scale, then in reservoir system.

    Possible options are:

(a) Ozonation of the water at the inlet of the reservoir and storage in the reservoir.

(b) Ozonation of the water at a certain point in the reservoir to allow long enough storage time for maximum DOC removal before other treatment proceses follow.

(c) Isolation of a certain section of the reservoir which can be used for preozonation and storage of water.

(d) Preozonation at the reservoir outlet and development of a fast biological process outside of the reservoir, in separate storage tanks, before other water treatment processes are applied.

(e) Use of Rotating Biological Contactors.

12. Final report on completion of project. Monthly progress reports are required.

TIMETABLE

1987 - 10 1989 - 12

RESOURCES

D.Bursill (10%), M.Drikas (30%), U.Kaeding (30%), G.Levay (100%)

AUSTRALIAN CENTRE FOR WATER TREATMENT AND WATER QUALITY RESEARCH

PROGRESS REPORT - JANUARY 1988

BIOLOGICAL REMOVAL OF ORGANICS

BACKGROUND

Organic compounds have been identified as a dominant factor in determining alum and chlorine dose rates in water treatment. The removal of organic material prior to other water treatment processes has the potential to remove taste and odour producing compounds as well as significantly reducing outlays in water treatment chemicals and minimising the production of disinfection by-products of public health concern.

The aim of this project is the removal of natural organic material by biological processes, using preozonation and then storing water or by using a medium such as activated carbon to support biological growth.

RESULTS

A research officer, G.Levay, was assigned to this project in October 1987. The rate of ozone decomposition in high purity water has been determined and the evaluation of optimum conditions for ozone generation and absorption in high purity water has begun.

Experimentation to develop a reliable and appropriate method for the determination of the biodegradable fraction of dissolved organic carbon in waters is also in progress. A reservoir sample was treated with 3.8 mg ozone per litre of water, innoculated with fresh water of the same origin and then incubated in the dark at 25°C for a period of 26 days. The DOC reduction during the total period was 20%, with 50% occurring in the first 4 days. Methods of increasing the biomass so as to decrease the time required to reach maximum organic carbon reduction are being investigated.

AWWARF Code #: AU-02

PROJECT DESCRIPTION

Please send reports to:

Mr. John B. Mannion
AWWA Research Foundation
6666 West Quincy Avenue
Denver, CO 80235

Project Title:

ORGANIC CARBON IN WATER, ITS SOURCES AND ROLE IN NUTRIENT TRANSPORT

Contact (name of person, organization, address, telephone):

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C/O DEPARTMENT OF SOIL SCIENCE
WAITE AGRICULTURAL RESEARCH INSTITUTE
GLEN OSMOND SOUTH AUSTRALIA 5064
TEL: (08) 372 2410

Project Description (Please attach a schematic diagram if appropriate):

The project aims to:

- Identify factors which control the release of organic carbon and phosphorus into water.
- Determine the associations between natural organics, nutrients (N & P) and clays and how these associations influence transport to reservoirs.
- Predict carbon and nutrient export from catchments under different management.

Two recent progress reports are attached.

Operating and cost data (including data on efficiency, results, etc.):

The current phase of the project is estimated to cost A$95,000. A further phase of this project is planned to commence in 1989, extending to 1992 at a cost of A$30,000 p.a.

Place(s) of installation/application (including dates):

Various catchment locations in the Mt Lofty Ranges, South Australia.

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

Funded by the Australian Government on the recommendation of the Australian Water Research Advisory Council.

C.S.I.R.O. Division of Soils (South Australia) will be associated with phase 2 of the project.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

THE AUSTRALIAN CENTRE FOR WATER TREATMENT AND WATER QUALITY RESEARCH

PROGRESS REPORT

PROJECT TITLE: Organic Carbon in Water, Its Sources and Role in Nutrient Transport

PROJECT LEADER: Prof. M. Oades
PROJECT OFFICER: Mr E. Cotsaris

INTRODUCTION

This project is a development of previous studies on natural organics in water and aims to identify factors which control the release of organic carbon and phosphorus into waters. The association between natural organics, nutrients (N & P) and inorganic matter (salts, clays and oxides) will be determined and used to assess their influences on transport of these materials to reservoirs. In determining these associations, concentration and fractionation techniques will be used. These fractions will be characterised in detail by spectroscopic techniques such as ^{13}C + ^{1}H NMR, I.R. and U.V.

Currently, analytical and preparative fractionation methods have been developed and some information on the character of natural organics and its association with nutrients (N & P) has been obtained.

ANALYTICAL FRACTIONATION METHOD

Of the different techniques available for the fractionation of aquatic humic substances, the method developed by J.A. Leenheer & E.W.D. Huffman (1979) was chosen as the most suitable. The method quantitatively classifies organic solutes into hydrophobic -base, -acid, and -neutral fractions and hydrophilic-base, -acid and -neutral fractions, based upon their adsorption upon nonionic and ion-exchange resin adsorbents. Initially work at the State Water Laboratory encountered significant technical difficulties, such as excessive resin bleed and poor reproducibility, which made the procedure unsatisfactory. However, further work has enabled these problems to be solved and some useful data has been obtained.

Samples were collected from the four chosen catchment areas: Myponga, Retreat Valley, Kangaroo Valley and Flamenco Park. The samples from Myponga were fractionated first, because of their characteristically high dissolved organic carbon (DOC) and phosphorus concentrations. A typical DOC fractionation analysis of Myponga is shown below.

Hydrophobic Solutes	Organic Carbon (mg/L)	% DOC
Total	3.14	39
Bases	0	0
Acids	1.84	23
Neutrals	1.30	16
Hydrophilic Solutes		
Total	5.01	61
Bases	0.79	10
Acids	3.71	46
Neutrals	0.51	6

The majority of the natural organics were fractionated as hydrophilic acids and hydrophobic acids.

CONCENTRATION OF ORGANICS

The fractionation of natural organics into hydrophilic an hydrophobic solutes is an artificial separation because it i. dependent on the resin's chemical behaviour. Consequently, a method of resin adsorption for the isolation of natural organics was developed for a detailed characterisation by spectroscopic techniques.

Excellent progress has been achieved in the concentration and isolation of the natural organics by an undergraduate student, Jeff Holman. The hydrophobic solutes have been isolated from two different Myponga samples. The hydrophilic solutes have been concentrated and presently require desalting for isolation. ^{13}C, ^{1}H and ^{31}P NMR and I.R. data are currently being collected from these samples for a detailed characterisation.

ASSOCIATIONS OF NUTRIENTS (N & P) WITH NATURAL ORGANICS

The associations of organic materials with phosphorus (P) and nitrogen (N) are unknown and basic information is required on their origins and their transfer to natural water. The combined effects of carbon and phosphorus are responsible for most of the chemical costs in water treatment. It is imperative to understand these associations as a basis for adequate control measures in catchments and water treatment. To this end, it was decided to subject a sample from Myponga to a DOC fractionation and determine the association of Carbon (C), Nitrogen (N) an Phosphorus (P) and the nature of the organic carbon in thes different fractions. The results are summarised in the table below.

Hydrophobic Solutes	% DOC	%TKN	$\%P_{tot}$
Total	42%	41	15
Bases	0	0	0
Acids	26	20	11
Neutrals	15	21	4
Hydrophilic Solutes			
Total	58	59	85
Bases	9	19	14
Acids	42	10	68
Neutrals	7	30	17

The Total Kjeldahl Nitrogen (TKN) is associated mainly with the neutral and basic fractions. This is expected since the hydrophilic, hydrophobic neutral and basic fractions are known to contain aliphatic and aromatic amines, amino acids, pyridines and amides. The Total Phosphorus (P_{tot}) is interestingly associated mainly with the hydrophilic solutes (85%) and very little with the hydrophobic solutes (15%).

COMPARISON OF RESIN FRACTIONATION AND ULTRAFILTRATION

The fractionation and concentration of natural organics by ultra-filtration is currently being investigated in collaboration with Waite Agricultural Research Institute. Some researchers have

reported results are dependent greatly on interactions between organic solutes and other constituents of the solution. These lead to the formation of aggregates and hence a higher estimation of molecular weight. Although natural organics are undergoing reactions all the time, their general overall characteristics should not change under ultrafiltration. We have validated this by using a concentrated sample from ultrafiltration and rediluting it to approximately its original DOC concentration. The rediluted sample, along with the original sample, was then subjected to the analytical resin fractionation. The results are summarised in the table below.

Hydrophobic Solutes	Original Sample % DOC	Rediluted Untrafiltration % DOC
Total	30	36
Bases	0	0
Acids	27	28
Neutrals	3	7
Hydrophilic Solutes		
Total	70	64
Bases	7	8
Acids	58	53
Neutrals	4	4

The concentration process invariably leads to changes in chemical factors which may modify the reactivity and structure of the compounds of interest, however the changes are so small that they are insignificant.

FLOW MEASUREMENT

The installation of gauging/sampling stations for examining water quality has been planned before the 1988 rainfall season. This has resulted in the evaluation of suitable flow meters, which have the capacity to measure and store flow data and activate an auto-sampler on a flow proportional basis.

The "Flo-Tote" by Marsh-McBirney, Inc. has been found to be accurate in flow measurement ± 5%, however it does not have the capacity to activate an auto-sampler. Other flow measuring devices are currently under consideration.

FUTURE WORK

Future work will initially involve the installation of gauging/sampling stations in at least two of the catchment areas. Success of the research project is highly dependent on the early installation of these stations in preparation for examining water quality in the 1988 rainfall season.

The concentration and fractionation of natural organic by adsorption chromatography will continue along with the development of new analytical techniques such as direct counter current chromatography, and bonding of organics with polyvinyl-pyrrolidone.

EMERGING WATER SUPPLY TECHNOLOGY **AWWARF Code #:** AU-03

PROJECT DESCRIPTION

Please send reports to:

Mr. John B. Mannion
AWWA Research Foundation
6666 West Quincy Avenue
Denver, CO 80235

Project Title:

THE REMOVAL OF TRIHALOMETHANES FROM WATER SUPPLIES BY ADSORPTION ON A SYNTHETIC RESIN MATERIAL

Contact (name of person, organization, address, telephone):

MR DON BURSILL
AUSTRALIAN CENTRE FOR WATER TREATMENT AND WATER QUALITY RESEARCH
PRIVATE MAIL BAG
SALISBURY SOUTH AUSTRALIA 5108

TEL: (08) 259 0236

Project Description (Please attach a schematic diagram if appropriate):

The project aims to develop a process for the removal of trihalomethanes from water supplies using a new material. This material appears to have fairly specific action for the trihalomethanes, but its chemistry can be readily modified to optimise extraction of other halogenated species (e.g. trichlorethylene).

Operating and cost data (including data on efficiency, results, etc.):

The project has only recently commenced but preliminary results indicate that trihalomethanes can be extracted at up to 95% efficiency with 1-2 minutes contact time. Indications are that the theoretical capacity of the material (approx. 10% of its weight) may be achievable. It is anticipated that the process will be able to be readily incorporated into existing water treatment plants or could be used as a point of use device.

Place(s) of installation/application (including dates):

Initial laboratory and pilot plánt studies based at the Australian Centre for Water Treatment and Water Quality Research.

Patent staus, if applicable:

Preliminary Patent applied for

Other information (e.g., funding source, cooperating agencies, etc.):

Currently internally funded

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

AUSTRALIAN CENTRE FOR WATER TREATMENT AND
WATER QUALITY RESEARCH

PROGRESS REPORT - JANUARY 1988

THM REMOVAL

BACKGROUND

Trihalomethanes are a by-product of chlorination of water supplies, particularly with waters of high organic content. These compounds are known carcinogens in rats and mice and as such are considered a health risk in water supplies. A material that can be cheaply manufactured has been found which adsorbs chloroform and other trihalomethane very efficiently. Because of this ability, and its insolubility in water, it was thought that this compound had great potential for removing chloroform and other trihalomethanes from water.

RESULTS

Stirring tests of Happy Valley water (approx. 200 ug/L trihalomethanes) with the material showed removal of approximately 20-30%.

Columns of the material mixed with an equal volume of alumina were prepared to facilitate filtration of the water. Removal efficiencies of 70-80% were obtained however blocking of the filters occurred rapidly. The material was then deposited via crystallization onto sand used in water filtration plant filters. Filtration of water in this manner proved much more effective but the retention time used was only 6 seconds and removal efficiency of 40-50% was obtained.

Further tests at the State Water Laboratory with retention times up to 1 minute were undertaken but removal efficiencies were only 10-20%. However the loading on the sand used in these later tests was only 1 mg/g sand compared to a fivefold stronger concentration used in previous tests.

Subsequent testing has resulted in extraction efficiencies of up to 95% with contact times of 1-2 minutes.

EMERGING WATER SUPPLY TECHNOLOGY **AWWARF Code #:** AU-04

PROJECT DESCRIPTION

Please send reports to:

Mr. John B. Mannion
AWWA Research Foundation
6666 West Quincy Avenue
Denver, CO 80235

Project Title:

THE REMOVAL OF NATURAL ORGANIC MATERIAL BY MAGNETIC BASED RESINS

Contact (name of person, organization, address, telephone):

MR DON BURSILL
AUSTRALIAN CENTRE FOR WATER TREATMENT AND WATER QUALITY RESEARCH
PRIVATE MAIL BAG
SALISBURY SOUTH AUSTRALIA 5108

TEL: (08) 259 0236

Project Description (Please attach a schematic diagram if appropriate):

A project has been completed, involving the development and evaluation of a magnetic based anion exchange resin for the removal of natural organics from water.

A subsequent project is planned to commence (as soon as funding is available) on pilot scale development of the process and further laboratory studies to improve the properties of the resin.

The magnetic resin when mixed with water presents a very high surface area to the water resulting in very good exchange kinetics for natural organics.

When mixing bases the fine particles of resin rapidly agglomerate under the influence of the magnetic forces and the material settles. The resin can be readily recovered and regenerated resulting in a dynamic ion exchange resin process.

Operating and cost data (including data on efficiency, results, etc.):

No costing yet available for the process.

Laboratory results indicate removal of 50% DOC can be achieved with approximately 90 minutes contact at relatively low "dose" rates. Removal up to 90% can be achieved with higher "dose" rates.

A progress report is available on request.

Place(s) of installation/application (including dates):

Laboratory experiments carried out at the Australian Centre for Water Treatment and Water Quality Research.

Pilot plant facilities located at Hope Valley (suburb of Adelaide, South Australia).

Patent staus, if applicable:

Patents held by C.S.I.R.O.

Other information (e.g., funding source, cooperating agencies, etc.):

Laboratory trials internally funded.

Funding required for pilot plant and further laboratory trials.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

EMERGING WATER SUPPLY TECHNOLOGY

AWWARF Code #: AU-05

PROJECT DESCRIPTION

Please send reports to:

Mr. John B. Mannion
AWWA Research Foundation
6666 West Quincy Avenue
Denver, CO 80235

Project Title:

A STUDY OF TROPHIC INTERACTIONS BETWEEN PROTOZOA AND ALGAE

Contact (name of person, organization, address, telephone):

MR B. ROBINSON
AUSTRALIAN CENTRE FOR WATER TREATMENT AND WATER QUALITY RESEARCH
PRIVATE MAIL BAG
SALISBURY
SOUTH AUSTRALIA 5108

TEL: (08) 259 0333 FAX: (08) 259 0228

Project Description (Please attach a schematic diagram if appropriate):

OBJECTIVES

To document the interactions of protozoa with algae which occur in Australian freshwater environments, to assess the impact of protozoa on algal populations and production, and to assess the feasibility of manipulating such interactions to contribute to control of algae in some circumstances.

PROGRESS

Early work has concentrated in two areas. Firstly, techniques are being developed for epifluorescent microscopy using chlorophyll autofluorescence and the fluorochromes FITC (to stain protein), DAPI and acridine orange (nucleic acids). Combinations of these stains should permit examination of whole cell structure, nuclear structure and division, and food vacuole contents. An advantage of fluorescent microscopy is that material can be fixed at the time of sampling; its treatment is not limited by the time required to examine fresh material. Secondly, literature is being collected as a basis for a review on protozoan/algal interactions and a data-base (cross-linking generic names of protozoa and algae) is being developed.

EMERGING WATER SUPPLY TECHNOLOGY **AWWARF Code #:** AU-06

PROJECT DESCRIPTION

Please send reports to:

Mr. John B. Mannion
AWWA Research Foundation
6666 West Quincy Avenue
Denver, CO 80235

Project Title:

DEVELOPMENT AND APPLICATION OF METHODS FOR DETECTING ENTERIC PROTOZOA IN WATER

Contact (name of person, organization, address, telephone):

MR B. ROBINSON
AUSTRALIAN CENTRE FOR WATER TREATMENT AND WATER QUALITY RESEARCH
PRIVATE MAIL BAG
SALISBURY
SOUTH AUSTRALIA 5108

TEL: (08) 259 0333 FAX: 259 0228

Project Description (Please attach a schematic diagram if appropriate):

Infections of man and animals by *Giardia* and *Cryptosporidium* occur widely in Australia. The extent to which these infections may be waterbourne is unknown.

OBJECTIVES:

Development of a method or methods for detecting *Giardia* and *Cryptosporidium* in water. Assessment of the potential role of water in transmission of enteric protozoans to man and between stock herds in Australia. Production of a simple handbook, useful to water microbiology laboratories through Australia. Assessment of control/disinfection measures. Assessment of survival of cysts or spores in the freshwater environment.

Project will commence shortly.

EMERGING WATER SUPPLY TECHNOLOGY **AWWARF Code #:** AU-07

PROJECT DESCRIPTION

Please send reports to:

Mr. John B. Mannion
AWWA Research Foundation
6666 West Quincy Avenue
Denver, CO 80235

Project Title:

A STUDY OF THE ECOLOGY OF AMOEBAE IN WATER SOURCES AND SUPPLIES

Contact (name of person, organization, address, telephone):

MR B. ROBINSON
AUSTRALIAN CENTRE FOR WATER TREATMENT AND WATER QUALITY RESEARCH
PRIVATE MAIL BAG
SALISBURY
SOUTH AUSTRALIA 5108

TEL: (08) 259 0333 FAX: 259 0228

Project Description (Please attach a schematic diagram if appropriate):

This project is concerned principally with the distribution and biology of two groups of free-living protozoa, *Naegleria* and *Acanthamoeba*, which are significant human pathogens.

OBJECTIVES

To determine the seasonal and geographic distribution of *Naegleria* and *Acanthamoeba* species in water, to understand the influence of environmental variables on their density and distribution and to identify potential sources of contamination of water supplies.

PROGRESS

Field studies have demonstrated seasonal succession of *Naegleria* species with different temperature requirements and cycles of population density in thermophilic species such as the pathogen *Naegleria fowleri*. Winter survival of *N. fowleri* depends on dormant cysts which may reach 10^3/gram dry weight of sediment. In the River Murray, seasonal occurrence of thermophilic *Naegleria* depends on flow phenomena as well as temperature.

Experimental study has concentrated on the influence of temperature on growth and transformation from amoebae to flagellates in *Naegleria* species. *N. fowleri* and its closest relative *N. lovaniensis* have almost identical temperature requirements for growth, but quite different kinetics of transformation and stability of the flagellate stage.

AWWARF Code #: AU-08

PROJECT DESCRIPTION

Please send reports to:

Mr. John B. Mannion
AWWA Research Foundation
6666 West Quincy Avenue
Denver, CO 80235

Project Title:

CONTROL OF AMOEBAE IN WATER SUPPLIES AND SWIMMING POOLS

Contact (name of person, organization, address, telephone):

MR B. ROBINSON
AUSTRALIAN CENTRE FOR WATER TREATMENT AND WATER QUALITY RESEARCH
PRIVATE MAIL BAG
SALISBURY
SOUTH AUSTRALIA 5108

TEL: (08) 259 0333 FAX: 259 0228

Project Description (Please attach a schematic diagram if appropriate):

This project is concerned principally with control of *Naegleria* and *Acanthamoeba*, which are significant human pathogens.

OBJECTIVES:

To determine the susceptibility of amoebae to various water treatment agents in vitro, to devise strategies for their control in water supplies and swimming pools and to monitor and assess control programs in the field where necessary.

PROGRESS:

The kinetics of action of chlorine and monochloramine against *N.fowleri* have been determined, as has the extent of inhibition of chlorine by cyanurate stabilization. The laboratory has been associated with successful implementation of chloramination in several rural water supplies.

A number of treatment agents used specifically in swimming pools have been tested, and surveys and trials of swimming pools and aerated spa pools conducted.

EMERGING WATER SUPPLY TECHNOLOGY **AWWARF Code #:** AU-09

PROJECT DESCRIPTION

Please send reports to:

Mr. John B. Mannion
AWWA Research Foundation
6666 West Quincy Avenue
Denver, CO 80235

Project Title:

A STUDY OF THE CONTRIBUTION OF PROTOZOA TO AESTHETIC PROBLEMS IN WATER QUALITY

Contact (name of person, organization, address, telephone):

MR B. ROBINSON
AUSTRALIAN CENTRE FOR WATER TREATMENT AND WATER QUALITY RESEARCH
PRIVATE MAIL BAG
SALISBURY
SOUTH AUSTRALIA 5108

TEL: (08) 259 0333 FAX: (08) 259 0228

Project Description (Please attach a schematic diagram if appropriate):

OBJECTIVES

To identify protozoans which may contribute odorous metabolites to water, to identify the metabolites concerned, and to assess the role of symbionts in producing the metabolites.

PROGRESS

Several isolates of *Saccamoeba* under study produce an odour tentatively identified by mass spectrometry as methyl isoborneol (MIB). Previously identified sources of MIB are all prokaryotes (actinomycetes or cyanophyte algae), and symbiotic bacteria within the amoebae are suspected as its immediate source in this case. In an unrelated group of amoebae, *Vannella*, three isolates produce a compound identified as geosmin. These isolates bear bacterial symbionts readily recognised by light microscopy; symbiont-free *Vannella* do not produce the odours.

AUSTRALIAN CENTRE FOR WATER TREATMENT AND WATER QUALITY RESEARCH

PROGRESS REPORT - APRIL 1988

BY-PRODUCTS OF DISINFECTION

BACKGROUND

This project aims to isolate and identify the by-products formed on disinfection of natural waters in South Australia. Interest in this area stems from concern over the suspected mutagenic/carcinogenic nature of compounds commonly formed in extracts of drinking water.

To date, the project has concentrated mostly on the by-products of chlorination, since chlorine is still the principal disinfectant used in South Australia. Some work has been done on chloraminated waters due to the increasing use of this method of disinfection and it is intended to pursue this study further in due course.

Isolation and concentration of the compounds of interest has been achieved using Closed Loop Stripping Analysis (CLSA) for volatile, non-polar organics and conventional liquid-liquid extraction for the less volatile fraction. The latter technique usually requires a derivatisation step to facilitate gas chromatographic analysis of acidic components. Identification of the unknowns is accomplished by gas chromatography/mass spectrometry.

RESULTS

The major products found in laboratory chlorination experiments and chlorinated water drawn directly from the distribution system were the trihalomethanes (THMs). Chlorinated South Australian waters contain relatively high levels of THMs by world standards due to the elevated levels of organic precursors present in the raw water. Highly coloured waters with dissolved organic carbon concentrations of up to 20 mg/L are not uncommon. Most of the remaining by-products occur at lower concentration than THMs, although comparable levels of di and trichlorinated acetones and acetic acids have been found on some occasions. Other halogenated ketones (C_3-C_5) and polychlorinated alkenes and alkanes have also been found.

The strong oxidising properties of chlorine leads to production of non-halogenated products, including carboxylic acids. A number of monobasic aliphatic acids has been identified, ranging from hexanoic to octadecanoic acid. Aromatic acids are less common but salicylic and benzoic acids have been found in chlorinated Fluka humic acid samples as oxidation products. When Fluka humic acid is oxidised with potassium permanganate, several additional benzene polycarboxylic acids are produced, as well as a significant number of dibasic aliphatic acids. Such compounds may also be present in chlorinated water but this has yet to be confirmed. Generally, chlorinated aromatics are not widespread in chlorinated water, although trichlorophenol, tribromophenol

and more recently dichloro-*p*-guaiacol and chlorobenzoic acid have been identified.

Recently, work has begun on analysis for the chlorinated furanone known as MX, which has been demonstrated to be a very potent Ames mutagen. The compound, 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone is isolated from chlorinated water on a mixed bed XAD resin column, concentrated and methylated prior to GC/MS analysis using single ion monitoring. Preliminary results of the first analysis were encouraging, with two large but unresolved peaks detected with the mass spectrometer tuned to m/e 147, which is the major ion in the mass spectrum of methylated MX. This may indicate the presence of this compound but the data is not conclusive at this stage. Further fractionation of the raw extract using HPLC may be required to positively identify this compound.

AUSTRALIAN CENTRE FOR WATER TREATMENT AND WATER QUALITY RESEARCH

PROGRESS REPORT - APRIL 1988

ODOURS IN WATER

BACKGROUND

The Centre's research project into odours associated with phytoplankton in waters is concerned with the identification of specific odorous chemicals which occur during blooms of algae in impounded water storages. Odorous compounds which find their way into the distribution system are a major cause of consumer complaint. Information on the chemical nature of odorants is therefore required to facilitate the development of methods for their control or removal. Through this work it may eventually be possible to chemically "fingerprint" specific algal genera, which may provide a means of "early warning" of an imminent algal bloom. Early detection of blooms may offer cost savings when dosing reservoirs with copper sulphate to control algal blooms.

RESULTS

The study of naturally occurring blooms is seasonal, with most activity taking place during the warmer summer months. Algal culturing procedures provide samples at other times of the year,, but there can be difficulties in growing some algae in artificial media. For example, there is no guarantee that a known odorous alga will produce any odour under culture conditions. Notwithstanding these limitations, a number of odorous compounds has been identified from both natural and cultured samples of several different algae. The Closed Loop Stripping method is used to concentrate volatiles prior to identification by gas chromatography/mass spectrometry.

Samples of the Cyanobacteria (blue-green algae), *Oscillatoria* sp. and *Anabaena flos-aquae* are usually characterised by a distinct earthy/grassy odour. Geosmin is the major odorant in these samples and is organoleptically perceptible at extremely low concentrations (ng/L) in water. Another compound, 2-methylisoborneol has also been identified and is a similarly potent earthy odorant. Several terpenoid compounds have been found in these samples but absolute identifications have not been possible due to the large number of isomeric possibilities and the paucity of analytical standards. One of these compounds however, gave an excellent visual mass spectral match with germacrene-D, which is related to the cadinenes and has also been reported as having an unpleasant grassy odour. Compounds of this kind also contribute to the overall odour character of the sample.

Bacterial decomposition of algal cells after the bloom has peaked leads to the production of several other compounds which alter the character of the odour over a period of time. Methyl butanol and a group of dimethyl polysulphides impart a putrid, rotting odour to the samples. One of these compounds, dimethyl trisulphide, has been responsible for "swampy" or "cooked vegetable" odours detected by consumers in Western Australian water supplies.

The blue-green algae *Microcystis aeruginosa* has an unpleasant smoky/mouldy odour which is due mainly to the presence of methylbutanol and -cyclocitral. Other minor components with pleasant odours include hexanol, 6-methyl-5-hepten-2-one and phenylethanol.

Synura petersenii, a Chrysophyte which blooms in the cooler months of late autumn to early winter has a cucumber-like odour. The *trans, cis* isomer of 2,6-nonadienal was identified as the cause of this odour.

Work is proceeding on large scale culturing of several algae to provide larger samples to assist in the identification of any further odorous compounds which may be present at lower concentrations.

AUSTRALIAN CENTRE FOR WATER TREATMENT AND WATER QUALITY RESEARCH

PROJECT STATUS REPORT - APRIL 1988

ALGAL TOXINS

This project is aimed at determining, by chemical analyses, levels of algal toxins in water.

Work to date has concentrated on reproducing a literature HPLC method for the determination of the *Microcystis* toxin. Large quantities of freeze-dried material were obtained following a bloom at Goolwa in 1987. A similar chromatogram to that reported was obtained and work will shortly be carried out to repeat this analysis with the fractions corresponding to the various peaks being obtained for toxicity testing. A non-toxic strain is being cultured for comparison.

This work has only a small allocation of resources at present but may become part of a larger program if applications for funds are successful.

AUSTRALIAN CENTRE FOR WATER TREATMENT AND WATER QUALITY RESEARCH

PROGRESS REPORT - APRIL 1988

EFFECTS OF PESTICIDE USAGE ON WATER QUALITY AND AQUATIC BIOTA

This project aims to determine the effects of intensive agricultural use of pesticides on water quality and the biota in the receiving waters. It specifically involves an investigation of the impact of the more recent, less persistent, but often more toxic pesticides and the determination of the effects of historical usage of persistent pesticides still present in the soils and stream sediments. An assessment of any deformities of chironomid larvae will be conducted and a correlation with pesticide usage will be tested.

This project has several aspects, viz.

1) A study of an area of intensive pesticide usage (Piccadilly Valley) to determine the extent of surface water pollution and effects on aquatic biota.

2) A similar study on the River Murray.

3) A study of groundwater contamination in an area of intensive horticulture (Virginia) by more mobile pesticides.

4) Development of analytical methodology for use in the above studies.

Most effort has been concentrated on the Piccadilly Valley but attempts have not yet been made to extend analytical methodology beyond the organo-chlorine insecticides. This has, however, enabled the detection of some pesticides apart from organo-chlorine insecticides, e.g. the herbicide chlorthal-dimethyl.

Water and sediment samples have been analysed on a more or less regular basis and have confirmed seasonal trends observed earlier. A paper on correlations between pesticide levels in sediments and chironomid deformities was prepared for publication. While there was some correlation, chironomids were absent from some locations recording the highest pesticide levels, perhaps indicating a lethal effect.

Samples of water were collected from one location following a sudden storm in December. These showed very high levels of suspended material (up to 9 g/L) with a number of pesticides present. Some were present at relatively high levels, e.g. chlorthal-dimethyl was present in one sample at a concentration of 110 ug/L. This confirmed earlier observations that heavy rainfall early in the summer season can cause severe erosion with large pesticide losses.

Water, sediment and biota samples were collected in early January. These were analysed to determine whether biota are accumulating pesticides from contaminated sediments. This work, undertaken by Dr Jayant Bapat while on sabbatical leave from

Chisholm Institute of Technology, showed fish to be highly contaminated with DDT levels far in excess of acceptable levels.

An application for funding for a project to study pesticides and chironomid deformities in the River Murray was unsuccessful. However, the Murray Darling Basin Commission decided to proceed with the collection and analysis of sediment samples to identify contaminated areas. Samples received from Victoria have been analysed but the extent of contamination was found to be negligible.

Sampling of the Virginia area has not yet commenced. Methodology for the determination of volatile fumigants has been evaluated and found to be satisfactory. As water is drawn from a confined aquifer and there is pressure for resources in other areas, only a few samples will now be analysed this summer. Depending on the outcome, this project may be extended next summer.

BELGIUM

BELGIUM

:Project Title:

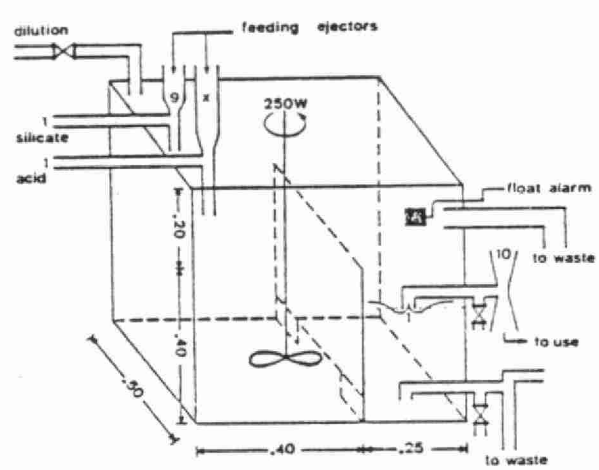
OPTIMIZATION OF CONTINUOUS GENERATION OF ACTIVATED SILICA

:Contact (name of person, organization, address, telephone):

Dr. W.J. MASSCHELEIN
Director of the Laboratories
Brussels Intercommunal Waterboard
Chaussée de Waterloo 764
B - 1180 BRUSSELS
(BELGIUM)

:Project Description (Please attach a schematic diagram if appropriate):

For the activation with sulphuric acid the contact time in the reactor volume must in all cases be kept between 6 and 25 % of the gelling time. Dosing parameters for the reactors are to foresee a reactor volume on the basis of an average concentration in the sol of 2 % SiO_2 of "neutral silicate" and a residence time of 15 - 20 % of the gelling time.
In the sulphuric acid activation of silicate with a continuous flow the auxiliary maturation or gelling vessel is quite unnecessary. The concentration in magnesium ions can influence secondary the gelling process.
An example is given of one of the reactor units able to produce an average quantity of 4 kg/h activated SiO_2 at the Tailfer plant.



Operating and cost data (including data on efficiency, results, etc.):

Installation : 1 million BF for 4kg/h reactor and control unit

Cost of chemicals : 200 BF per kg activated SiO_2

Place(s) of installation/application (including dates):

TAILFER plant of the BRUSSELS' INTERCOMMUNAL WATERBOARD

Patent status, if applicable:

open

Other information (e.g., funding source, cooperating agencies, etc.):

If available attach descriptive publications, technical literature, manufacturers' specification, patent descriptions, etc.

PROJECT DESCRIPTION

Project Title:

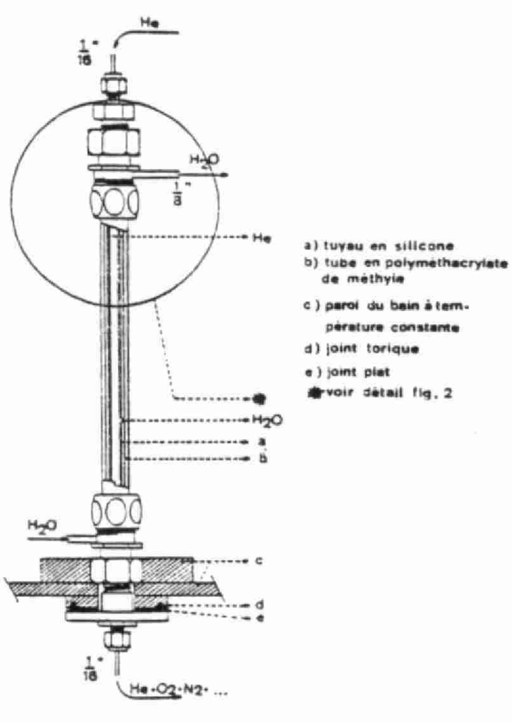
DEVELOPMENT OF AN INSTRUMENTAL METHOD
FOR DIRECT DETERMINATION OF DISSOLVED NITROGEN

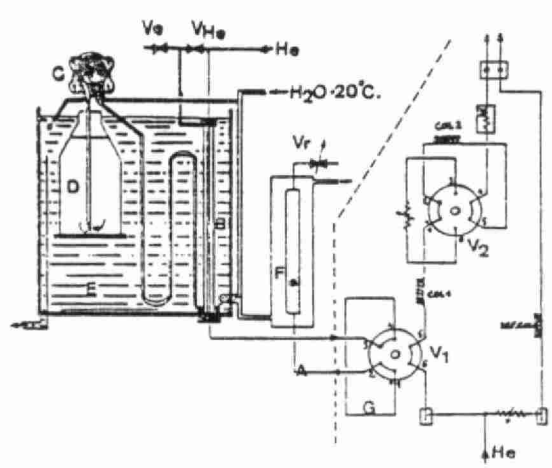
Contact (name of person, organization, address, telephone):

Dr. W.J. MASSCHELEIN
Director of the Laboratories
Brussels Intercommunal Waterboard
Chaussée de Waterloo 764
B - 1180 BRUSSELS
(BELGIUM)

Project Description (Please attach a schematic diagram if appropriate):

Development of an extraction method making able the direct determination of dissolved nitrogen in water with gas chromatography after extraction. The method is carried out on circulating gaseous helium inside a suitable silicone rubber tube plunged into a water layer which is circulated countercurrently to the helium in a glass or methyl-polymethylacrylate tube. The method is based on the gas transfer through a silicone membrane; the driving force is the partial pressure difference. The standard deviation is of 0.2 mg/l N2 (schematics joined).





Operating and cost data (including data on efficiency, results, etc.):

Detection limit : 0.5 mg = dynamic range : 200 x

Cost of instrument : ± 1 million BF

Place(s) of installation/application (including dates):

HAVRE station of the BRUSSELS' INTERCOMMUNAL WATERBOARD

Patent status, if applicable:

open

Other information (e.g., funding source, cooperating agencies, etc.):

paper joined (in French)

If available attach descriptive publications, technical literature, manufacturers' specification, patent descriptions, etc.

SCIENCES DE L'EAU, 5 (1986) 169-184

Méthode directe de détermination de l'azote dissous

Direct method of determination of dissolved nitrogen

G. MINON et W.J. MASSCHELEIN*

Résumé

La diffusion, au travers d'une membrane en silicone, couplée à la chromatographie en phase gazeuse, permet le dosage de l'azote dissous dans l'eau. Cette mesure s'avère être de première importance dans l'étude des équilibres des gaz dissous, tout comme dans l'approche des rendements de "dissolution-dégazage" envisagés pour l'emploi d'un gaz enrichi en oxygène.

Dans la méthode développée ici, un écart-type de 0,08 mg/l et 0,17 mg/l caractérise respectivement les mesures de concentration d'oxygène et d'azote proches de la saturation par rapport à l'air. La gamme dynamique de la méthode s'étend à 200 fois au moins.

L'utilisation de la technique mise au point révèle la tendance à la sursaturation des eaux en azote, de même que la lenteur du dégazage de celui-ci.

Summary

Diffusion through a silicone membrane, coupled with gas chromatography enables to determine dissolved nitrogen in water. The measure of this concentration is of utmost importance in the study of equilibria between the gas vs. the liquid phase and also in the evaluation of the dissolving-degassing yields when using a gas phase enriched with oxygen.

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* Laboratoires de la Compagnie Intercommunale Bruxelloise des Eaux - Chaussée de Waterloo 764 - B-1180 - BRUXELLES (Belgique).

The method as developed in this contribution is characterised by a standard deviation of 0.08 mg/l and 0.17 mg/l respectively for dissolved oxygen and nitrogen at concentrations near the levels of saturation vs. air. The dynamic range of the direct method is of at least 200.

Direct determination of dissolved nitrogen as developed here, provides good evidence of the over-saturation in nitrogen as well as the point that the degassing of the latter is a slow process.

1 - INTRODUCTION

L'aération sous pression, en vue d'enrichir ou de saturer l'eau en oxygène, peut conduire à une sursaturation en azote si un abaissement de pression succède à ce traitement. Différents effets et perturbations peuvent en résulter (ALBRECHT, 1974 ; MEVIUS, 1980 ; WEITKAMP et KATZ, 1980 ; BILSTAD, LIGHTFOOT et POLKOWSKI, 1978).

Les Etats de Washington et de l'Orégon auraient fixé, respectivement à 110 et 105 % de la saturation à la température considérée, les limites de sursaturation permises en azote dans les eaux à destination piscicole (LIGHTFOOT et POLKOWSKI, 1978). D'autres chiffres sont commentés (WEITKAMP et KATZ, 1980) et l'Agence de Protection de l'Environnement des U.S.A. défend des valeurs de 110, 115 ou 120 % (WEITKAMP et KATZ, 1980).

Dans un autre ordre d'idées, l'oxygène pur, utilisé en lieu et place d'air, peut être associé à différents avantages, tant dans le domaine des eaux potables que des eaux résiduaires (ALBRECHT, 1974 ; MEVIUS, 1980 ; An., 1975). L'utilisation de l'oxygène provoque un changement des conditions d'équilibre de dissolution des gaz, conséquence de la modification de l'atmosphère équilibrante. Un dégazage d'azote en est la résultante (MASSCHELEIN, 1976). Par ailleurs, la littérature ne mentionne pratiquement pas de données quantitatives concernant la "performance" atteinte dans le dégazage de l'azote au départ d'une eau saturée en ce gaz et traitée par un dispositif d'oxygénation.

2 - BUT DE CETTE RECHERCHE

Il sera fait appel à la diffusion au travers du caoutchouc silicone pour réaliser un appareillage destiné à la détermination de l'azote dissous.

3 - PRINCIPE DES MÉTHODES ANTÉRIEURES

Avant 1968, quatre possibilités (TOLK, LINGERAK, KOUT et BORGER, 1969) sont décrites :

a) l'injection directe de l'eau sur une colonne préliminaire ;

b) l'ébullition préparatoire ;

c) l'extraction des gaz sous vide ;

d) l'entraînement par barbotage du gaz porteur.

Souvent la mise en oeuvre de ces techniques nécessite une dessication avant l'injection sur les colonnes de séparation (KILNER et RATCLIFF, 1964 ; WEISS et CRAIG, 1973 ; GAMO et HORIBE, 1980). La dessication s'accompagne souvent d'un volume de prise d'échantillon limité à quelques ml, alors que l'entraînement par barbotage du gaz porteur permet de développer des appareils pour extraction en continu (WALKER et FRANCE, 1969 ; WILLIAMS et MILLER, 1962).

Deux variantes peuvent s'ajouter aux méthodes précédentes (LEGGET, 1979 ; BOUCK, 1982 ; D'AOUST, WHITE et SEIBOLD, 1975 ; FICKEISEN, SCHNEIDER et MONTGOMERY, 1975 ; BILSTAD, 1978 ; KOLLIG, FALCO et STANCIL, 1975 ; BILSTAD et LIGHTFOOT, 1982) :

1) établir un équilibre d'échange entre l'eau et un petit volume gazeux ;

2) faire diffuser les gaz dissous au travers de membranes.

Le SILASTIC* est le matériau généralement employé. La méthode décrite ici vise plus spécialement à augmenter la sensibilité et de permettre l'analyse en laboratoire d'échantillons prélevés sur site et transportés.

4 - MATÉRIEL ET MÉTHODES

4-1 Matériel

La construction de l'appareillage utilisé comme analyseur est illustré par les figures 1 et 2.

Comme le montre le détail d'une extrémité du montage *(figure 2)*, le tuyau de caoutchouc silicone translucide de 15 cm de long, de 3 et 5 mm de diamètre intérieur et extérieur respectivement, de marque VERSILIC**, est maintenu dans un tube en méthacrylate de 15 cm de long, d'un diamètre intérieur de 7 mm et de 1,5 mm d'épaisseur, par serrage sur un bout de tube de polypropylène et ce de manière à créer un conduit à double paroi, grâce à deux bagues de centrage cannelées. L'échangeur est fixé dans un bain à thermostat.

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* Caoutchouc silicone DOW CORNING CORPORATION, MIDLAND, MICHIGAN 48640.

** VERSILIC, Manufacture générale de caoutchouc VERNERET S.A., 39 rue Pierre et Marie Curie, F-94203 IVRY-SUR-SEINE.

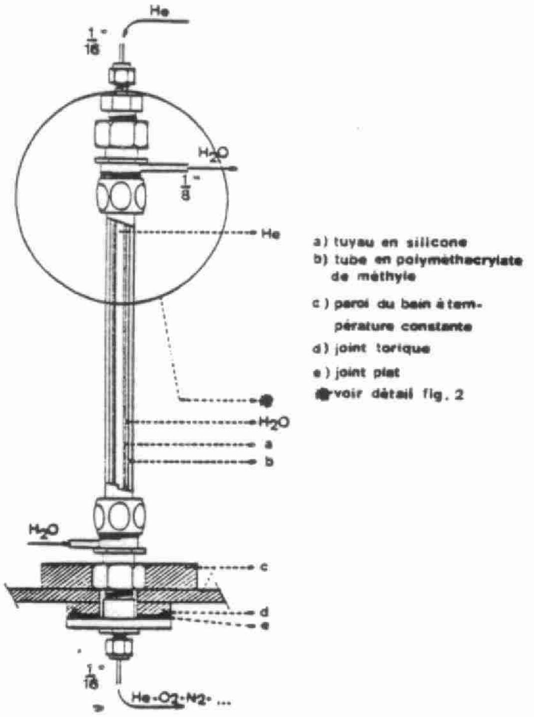

Figure 1
Schéma de l'échangeur

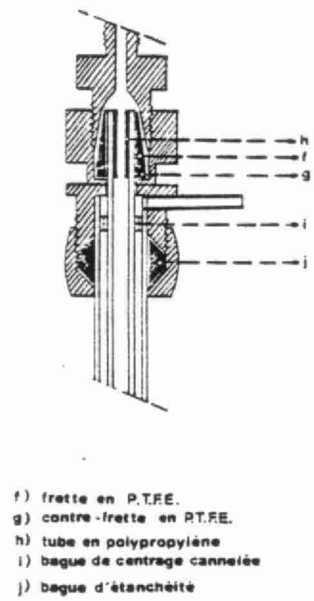

Figure 2
Détail de la figure 1

L'intérieur du tuyau en polysiloxane est balayé de haut en bas par un courant d'hélium entrant dans la boucle de la prise d'essai (capacité : 1 ml) montée sur la vanne d'injection d'un chromatographe en phase gazeuse CARLE 111* équipé de trois colonnes :

- colonne 1 : 8' - 80 % Porapak N - 20 % Porapak Q, 50/80 mesh ;
- colonne 2 : 6' - tamis moléculaire 5A, 42/62 mesh ;
- colonne 3 : 6' - 8 % ov-101 sur chromosorb WAWDMCS 80/100 mesh.

Le débit de passage de l'hélium est ajusté par une vanne de réglage et contrôlé par un débitmètre de précision. L'eau à analyser est pulsée de bas en haut, entre le tuyau "VERSILIC" et le méthacrylate, par l'intermédiaire d'une pompe péristaltique de type MASTERFLEX à variateur et inverseur de débit. La tête de dosage n°7014 est équipée d'un tuyau en "Tygon" n°6408-43, de diamètre intérieur et extérieur de 0,79 mm et 4,1 mm respectivement, et d'une longueur de 20 cm. La tête est légèrement modifiée par l'insertion d'une piste, tuyau de cuivre à l'intérieur duquel circule l'eau du bain. Le tuyau en "Tygon" est en contact permanent avec cette piste qui assure le maintien de la température lors du transfert de l'échantillon d'eau à analyser.

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* CARLE INSTRUMENTS, 1200 Knollwood Circle, ANAHEIM, CA 92801.

Le débit d'hélium peut être partiellement dérivé dans le circuit d'eau par le jeu de deux vannes "tout ou rien", V_s et V_{He}, comme indiqué dans la figure 3.

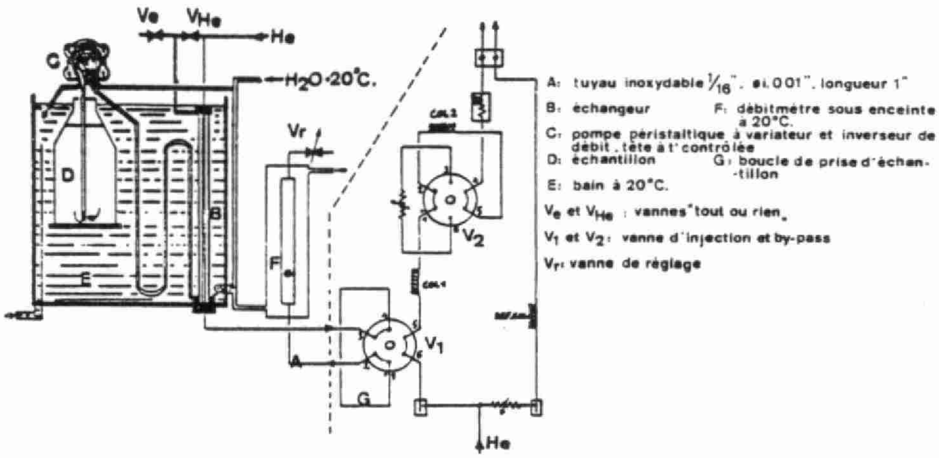

Figure 3

Schéma de principe du montage de l'échangeur dans le circuit d'analyse

Chromatographe CARLE modèle 111

4-2 Appareillages complémentaires

Le chromatographe est alimenté en hélium au débit de 26 ml/min pour une pression de 3,7 bars et une température du four de 98°C. Nous avons employé un enregistreur CHROMATOPAC CR_1B SHIMADZU.

4-3 Discussion de la linéarité

4-3-1 Choix des paramètres de travail

L'interaction des valeurs de débit, pression, volume, durée d'échange et température, nécessite un choix initial.

La température du bain : la sélection à 20°C se justifie par la facilité de préparation des échantillons d'eau saturée, destinés à l'étalonnage.

La pression d'hélium dans le circuit d'échange : la relation entre la surface des pics et la pression d'hélium étant linéaire *(figure 4)*, la valeur de 0,5 bar a été choisie comme pression d'utilisation.

Le débit d'hélium dans l'échangeur : 4 ml/min ; un débit plus élevé amène une perte de sensibilité, un débit inférieur pose des problèmes de réglage *(figure 5)*. Il est à noter que ce point est déterminant pour la reproductibilité des mesures.

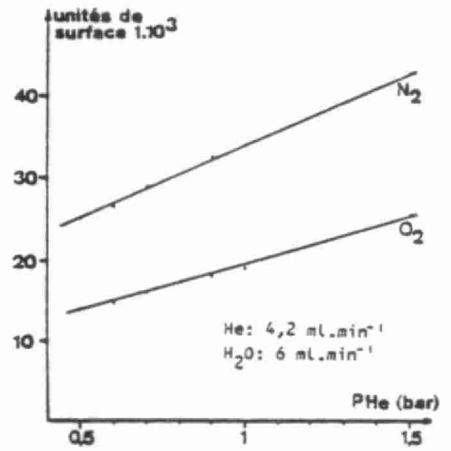

Figure 4
Réponse en fonction de la pression

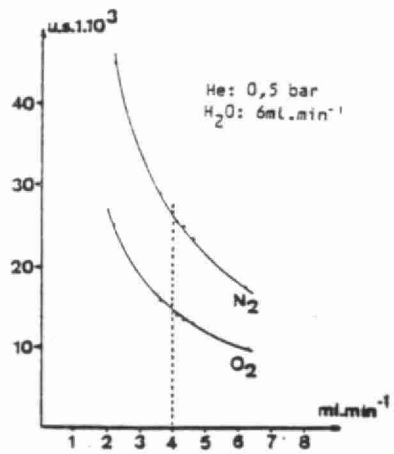

Figure 5
Réponse en fonction du débit d'hélium

Durée d'échange : 15 minutes *(figure 6)*.

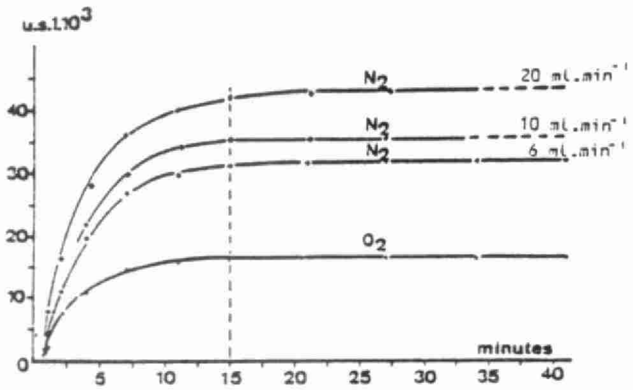

Figure 6
Réponse en fonction de la durée d'échange

Le débit d'eau à échanger : 6 ml/min, un débit supérieur n'apporte qu'une augmentation de sensibilité marginale *(figure 7)*. De plus, à cette valeur correspond une très bonne tenue du "Tygon".

Elimination des gaz résiduaires : On procède obligatoirement par purge et balayage à l'hélium après chaque essai.

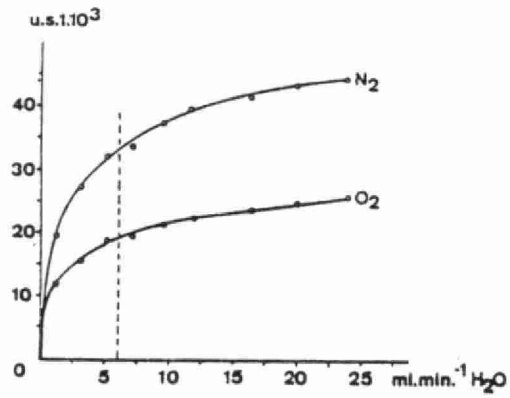

Figure 7
Réponse en fonction du débit d'eau

4-3-2 Etalonnage

L'étalonnage est à effectuer au moins une fois par jour (WEISS et CRAIG, 1973). Il peut se faire au moyen d'un ou de deux standards externes.

Echantillon d'eau saturée servant de seul standard externe :
La température du bain et du laboratoire étant à 20°C, la réalisation rapide d'échantillons d'eau saturée se fait grâce à une adaptation du dispositif prévu par FOX (FOX, 1909), utilisé par WORTHINGTON et repris par GRASSHOFF (GRASSHOFF, 1964) (voir *figure 10*).

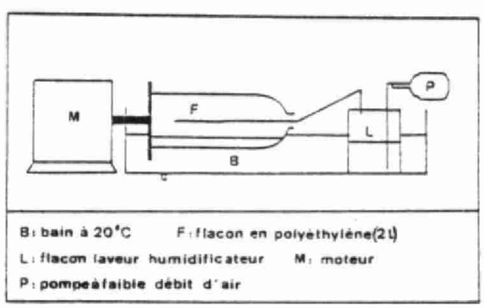

Figure 8
Appareillage pour la saturation de l'eau par rapport à l'air

Un volume de 280 ml d'eau distillée est introduit dans le flacon en polyéthylène et ce dernier est mis en rotation.

Interférences, linéarité et passage par l'origine :

- Cas de l'oxygène

La courbe étalon établie par comparaison aux dosages selon WINKLER (*figure 9*) ne passe pas par l'origine.

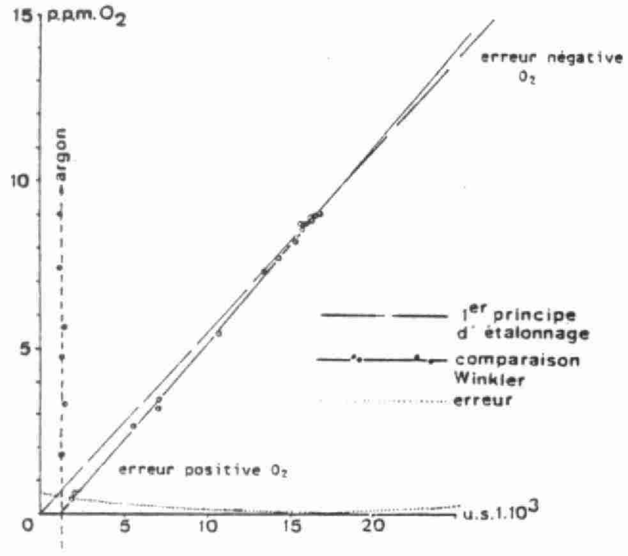

Figure 9

La valeur à l'origine correspond à la réponse de l'argon (WILLIAMS et MILLER, 1962 ; LEGGET, 1979 ; ELSEY, 1959 ; SWINNERTON *et al.*, 1962 ; REUSMANN, 1968). Cette erreur de mesure due à l'argon n'a pas toujours été prise en considération dans la littérature (BILSTAD et LIGHTFOOT, 1982 ; ROPARS, 1968 ; SUTTER, 1971).

Le premier principe d'étalonnage ne peut donc s'utiliser que pour des teneurs en O_2 proches de la valeur de saturation : 9 ± 2 mg/l.

La procédure d'étalonnage à deux standards externes est préférable. Le premier standard est de l'eau saturée ($\frac{O}{N}$ = 0,56) et le second le liquide au-dessus du précipité d'un essai WINKLER (valeur 0). Ce procédé permet d'éviter les corrections par calcul ou des modifications très importantes destinées à séparer et mesurer l'argon (LARD et HORN, 1960 ; VIZARD et WYNNE, 1959 ; SWINNERTON *et al.*, 1962).

- Cas de l'azote

Il n'y a pas d'interférence. Les échantillons doivent répondre à la règle obligatoire du rapport 0,56 < $\frac{O}{N}$ < 0,57 (*figure 10*).

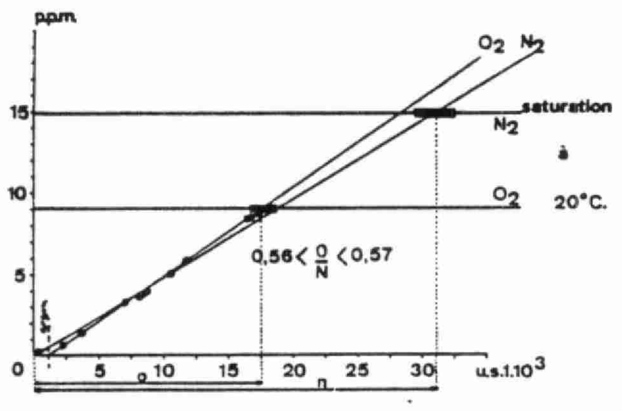

Figure 10
Etalonnage

En effet, il découle du principe de la détection par conductivité thermique :

$$\frac{O}{N} = \frac{(O_2' + Ar') \;.\; [(\frac{O_2'}{O_2' + Ar'} \;.\; \lambda\, O_2) + (\frac{Ar'}{O_2' + Ar'} \;.\; \lambda\, Ar)]}{N_2' \;.\; \lambda\, N_2} = 0{,}5629$$

où

O = unités de surface mesurées pour O_2 + Ar,
N = unités de surface mesurées pour N_2,
N_2' , O_2' , Ar' = solubilités des gaz en ml/l à 20°C et pour l'air saturé en eau à pression atmosphérique,

N_2' = 11,92 ml/l à 20°C,

O_2' = 6,36 ml/l à 20°C,

Ar' = 0,31 ml/l à 20°C,

et

$\frac{N_2}{Ar'}$ = 39, 08 ml/l à 20°C = conductivité thermique des gaz respectifs :

Ar = 3,908 cal/ml,

O_2 = 5,732 cal/ml,

N_2 = 5,86 cal/ml

N_2' et O_2' sont données par MURRAY (MURRAY *et al.*, 1969).

Ar' est obtenue à partir des données de BENSON et PARKER (1961).

La présente mise au point *(figures 9 et 10)* confirme la linéarité déjà établie (BILSTAD et LIGHTFOOT, 1982).

Selon les données rapportées par GALLETTI *et al.*, (1966), les quantités maximales des gaz diffusibles par notre échangeur s'établissent à :

Oxygène = 118 mg O_2/l ;
Azote = 193 mg O_2/l.

Selon DRISCOLL (1976), la conductivité thermique permettrait une détection linéaire de 10^5, soit de 1.10^{-1} à 1.10^6 µg. C'est donc le montage du "VERSILIC" qui est limitatif.

5 - PRÉCISION ET SENSIBILITÉ

Compte tenu d'un étalonnage journalier, la méthode permet une précision de 9,08 ± 0,08 mg/l O_2 ; 14,89 ± 0,17 mg/l O_2.

Les limites de détection se situent à 0,05 mg/l O_2 et 0,07 mg/l N_2.

6 - EXEMPLES D'APPLICATION - ANALYSE D'ÉCHANTILLONS PRÉLEVÉS SUR LE TERRAIN

6-1 Les installations de Spontin et de Crupet sont essentiellement constituées de galeries drainantes creusées dans le calcaire carbonifère. Elles captent les eaux d'infiltration provenant de nappes libres. La profondeur de captage oscille autour de - 10 m. Les eaux analysées ont été prélevées en différents points.

Les analyses révèlent un léger déficit en oxygène dissous. Il est compris entre - 3 et - 5 mg O_2 par rapport à la valeur de saturation par l'air à la pression normale. Ce déficit se manifeste aux sites qui marquent une vulnérabilité bactériologique fréquente. En ce qui concerne l'azote, il convient de relever une certaine tendance à la sursaturation. La valeur est de + 3 mg/l N_2 et atteint + 6 mg par endroit *(figure 11)*.

6-2 Le captage de Vedrin collecte les eaux d'infiltration qui s'écoulent librement dans les galeries d'une ancienne exploitation de minerais de fer (marcassite). Les eaux captées à - 130 m de profondeur sont remarquablement exemptes de matières organiques (TOC < 1 mg/l). Les bactéries y sont pratiquement absentes et aucun indice de pollution fécale ne fut constaté au cours de 25 ans d'exhaure. Cependant, à l'exception des endroits en regard des puits d'accès (n°s 5 et 16), le manque d'oxygène dissous se manifeste de manière générale. Il est de - 9 mg/l O_2, soit une concentration moyenne effective de l'ordre de 3 mg/l. Soulignons toutefois la variation, de 1,5 à 8,0 mg/l O_2, qui correspond à un déficit situé entre - 10 et - 3 mg/l. Ce dernier, envisagé comme une consommation par l'oxydation, serait associé à la transformation *in situ* des sulfures en sulfates de fer. Pour une teneur moyenne des eaux de 3 mg/l de fer, un déficit en oxygène de 5 mg/l paraît possible ; mais une partie du fer dissous peut se trouver sous forme d'hydrogénocarbonate, entraînant des situations ponctuelles de drainage ferrugineux, susceptibles de s'écarter significativement de la moyenne.

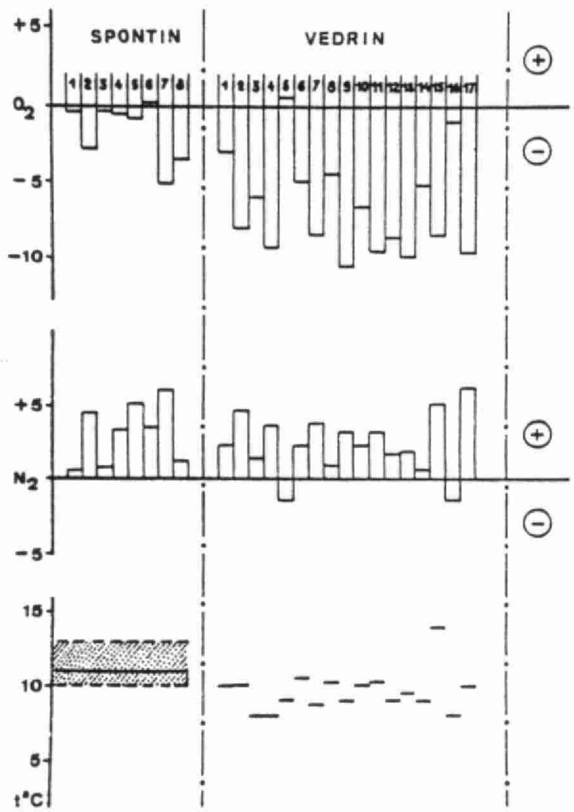

Figure 11
Gaz dissous dans les eaux à nappe libre

Pour ce qui est de l'azote dissous, l'écart moyen excède la concentration à saturation de + 3,2 mg/l, les valeurs extrêmes se situant à + 1 et + 6 mg/l. La sursaturation en azote est donc du même ordre de grandeur pour ce captage que pour ceux réalisés dans les galeries du carbonifère *(figure 11)*.

6-3 Nos captages dans la région montoise regroupent les eaux d'un ensemble de puits foncés dans le crétacé. Leur profondeur est de ± 90 m. Le sous-sol comprend une couverture tourbeuse superficielle de plusieurs mètres (jusqu'à ± 5 m par endroit). Munies de crépines, les pompes, immergées en moyenne à - 40 m du sol (sauf G_3 : - 31 m), refoulent les eaux en surface dans des conduites sous pression.

Pour l'ensemble des puits de cette zone, les eaux se montrent pauvres en oxygène. Pendant les périodes d'arrêt, ce phénomène s'aggrave. L'excès en azote voisine les + 7 mg/l par rapport à la valeur de saturation par l'air atmosphérique. Cette richesse est donc légèrement supérieure à celle relevée dans le cadre des captages à écoulement libre. Il est à noter qu'il subsiste, en permanence, plusieurs mètres de colonne d'eau sur la crépine d'aspiration des pompes (hauteur variable entre 15 m et 34 m, selon les rabattements de la nappe aquifère).

L'aération par injection d'air comprimé au fond des puits à raison de ± 0,015 Nm^3 par m^3 d'eau exhaurée, ramène entre - 5 et - 7 mg/l le déficit en oxygène par rapport à la saturation par l'air à la pression

atmosphérique *(figure 12)*, ce qui porte entre 4 et 6 mg/l la concentration effective et garantit une composition d'eau mettant les conduites d'adduction à l'abri de corrosions anaérobiques. Lors de cette injection en profondeur, il convient de remarquer que la concentration en azote dissous s'accroît de + 3 à + 6 mg/l selon le cas. La sursaturation atteint donc couramment 10 mg/l à l'exhaure.

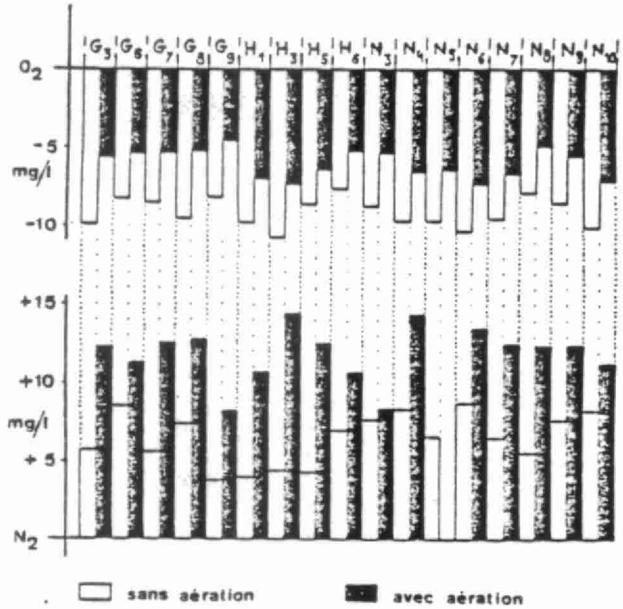

Figure 12
Gaz dissous dans les eaux du crétacé (Mons)

6-4 En conclusion, il apparaît que la plupart des eaux des nappes souterraines envisagées sont sursaturées en azote dissous par rapport à la concentration équilibrante vis-à-vis de l'air. Le dégazage libre de l'azote de l'eau s'avère être un phénomène lent. L'aération par injection d'air sous pression accroît la sursaturation dont il faut, dès lors, tenir compte dans les bilans de matières. L'investigation en est désormais possible grâce à la méthode analytique développée ci-dessus.

- Remplacer l'air par un gaz enrichi en oxygène dans la génération d'ozone par décharge électrique permet d'en augmenter la production au moyen des mêmes équipements (MASSCHELEIN, 1976 ; MASSCHELEIN, 1977 ; MASSCHELEIN, 1980). Cette pratique conduit au dégazage de l'azote dissous et à la sursaturation en oxygène de l'eau soumise à l'injection du gaz contenant l'ozone.

- Les résultats du dégazage d'azote peuvent être exprimés *(figure 13)* en considérant comme 100 % les trois valeurs types suivantes pour l'ozone dissous dans l'eau au départ :

19,05 mg/l, concentration équilibrante à 7°C par rapport à l'air,

20,8 mg/l, concentration mesurée dans l'eau avant ozonation,

23,7 mg/l, concentration mesurée dans l'eau après dispersion d'air (voir *tableau 1*).

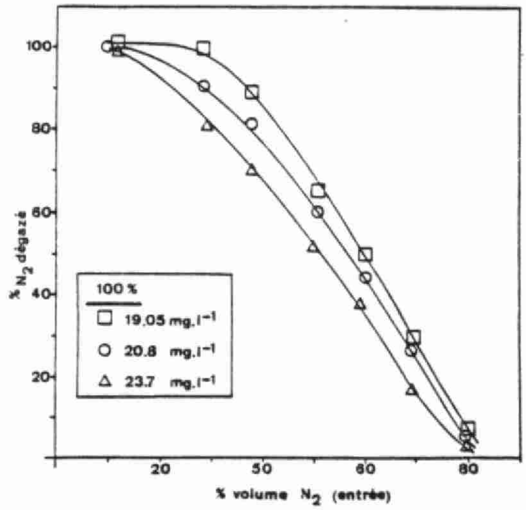

Figure 13
Dégazage d'azote par dispersion de gaz enrichi en oxygène

Tableau 1
Teneurs d'oxygène et d'azote en solution et en phase gazeuse

% O_2 gaz entrée	% O_2 gaz sortie	Nm^3/h gaz	mg/l O_2 dissous	mg/l N_2 dissous	CONDITIONS
20,6	20,1	312	15,7	23,7	Q eau : 2750 m^3/h t° eau : 7°C
31	27	314	20,6	21,2	Poids spécifique N_2 : 1,218 kg/m^3
40,8	33,6	294	25	18,9	
50	41	312	27,8	16,1	Hauteur de colonne d'eau au point de prélèvement : - 3,56 m
62,2	50,4	322	34,8	12,6	
71,4	57,8	326	37,8	10,3	
88,6	72,4	336	43,9	6	Concentration en solution avant ozonation : N_2 : 20,8 mg/l O_2 : 12,6 mg/l

Dès que la concentration en oxygène du gaz injecté dépasse 30 % en volume, les données confirment que le dégazage de l'azote n'est que partiel par rapport au(x) valeur(s) d'équilibre.

- Les valeurs des concentrations en gaz dissous doivent être interprétées, par rapport aux concentrations à l'équilibre, aux pressions respectives de 1,386 bar en bas et 1,03 bar en haut des colonnes de rétention *(figure 14)*. Par comparaison à la composition du gaz à l'injection, les concentrations en O_2 et N_2 dissous se situent dans des valeurs intermédiaires à la saturation à 1,386 bar et à 1,03 bar respectivement.

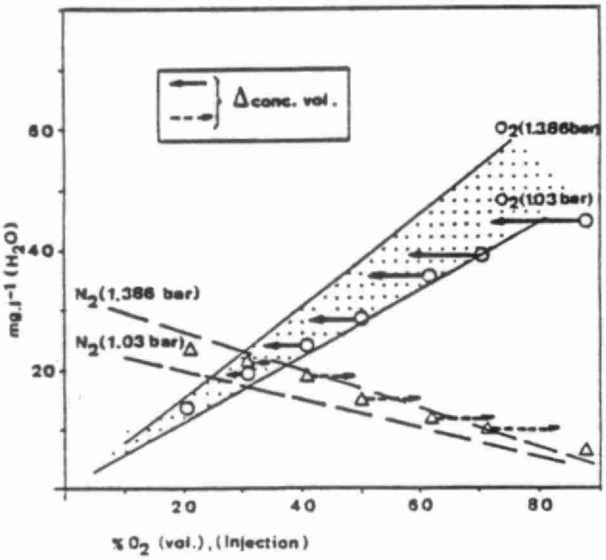

Figure 14
Appauvrissement en oxygène (←□) et enrichissement en azote (Δ→) du gaz échangé avec l'eau

Si on considère la composition du gaz à l'évent, les concentrations mesurées dans l'eau à la surface d'échange libre révèlent donc une sursaturation par rapport aux valeurs d'équilibre à 1,03 bar.

En conclusion, l'atmosphère aux évents (points terminaux des flèches horizontales dans la figure 14) est enrichie en azote et appauvrie en oxygène par rapport au gaz à l'entrée.

7 - Conclusions

La détermination simultanée de l'oxygène et de l'azote dissous dans l'eau est possible par une technique de diffusion au travers d'une membrane en silicone, suivie d'une analyse chromatographique du gaz diffusé. Parmi les paramètres d'optimisation de la méthode, il est nécessaire de citer la pression du gaz échangeur (He à 0,5 bar), le débit de ce gaz (ici 4 ml/min), le débit et la durée de circulation d'eau à analyser.

Pour l'étalonnage, il peut être fait usage d'une solution saturée par rapport à l'air, tant pour l'azote que pour l'oxygène. Ce dernier, cependant, peut être l'objet d'une interférence due à l'argon. L'écart par excès ou par défaut de 0,5 mg/l peut être corrigé par l'analyse d'un blanc diffusé à partir du liquide subsistant au-dessus du précipité d'un test selon WINKLER.

Au voisinage de la concentration saturante, la précision est de ± 0,08 mg/l pour l'oxygène et de ± 0,17 mg/l pour l'azote. Les limites de détection sont de 0,05 mg/l et 0,07 mg/l respectivement.

Appliquée aux eaux souterraines, la méthode a mis en évidence une sursaturation en azote dissous que le captage soit du type à nappe libre ou du type à nappe profonde.

Cette situation subsiste indépendamment de la déficience en oxygène dissous. Le dégazage spontané de l'azote est un phénomène lent.

L'aération en nappe profonde accroît la sursaturation en azote parallèlement à la hausse de concentration en oxygène dissous.

En cas d'injection d'un gaz enrichi en oxygène par rapport à l'air, il se confirme que le dégazage d'azote en sursaturation n'est que partiel.

Outre les applications faites dans cette étude, la technique par diffusion développée offre des perspectives pour d'autres gaz dissous et dans d'autres situations analytiques. Citons le CO_2 à titre d'exemple.

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PROJECT DESCRIPTION

Project Title: **S.V.W. Project A/022:**

Comparative Study of Activated Nitrification in a Fluidised Bed and Expanded Bed Reactor

Contact (name of person, organization, address, telephone):

S.V.W. - Studiecentrum voor Water
ir. J.G. Janssens - Scientific Coordinator
p/a A.W.W., Mechelsesteenweg 64
B-2018 Antwerpen
Tel. (03)238.78.30

Project Description (Please attach a schematic diagram if appropriate):

Waste water effluents often contain considerable amounts of residual ammonium. The latter constitutes a threat to fish. Biological removal by nitrification is a possible solution.

Two new approaches to achieve intensive and stabile nitrification were examined. The first method is based on a fluidised bed system, aerated in a conventional two-phase mode with sand as carrier material. Air is used to aerate. This imposes a high recirculation rate of the water. Due to the high conversion rates, the reactor can be very small and preferably shallow and wide. Techniques to select active nitrifying microbial consortia have been developed.

The second method makes use of polyurethane sponges as a carrier material. The expanded bed system has a very short start-up period compared to the fluidised bed. However, the conversion rates are lower due to diffusion and transport limitations through the matrix.

Operating and cost data (including data on efficiency, results, etc.):

Selected microbial consortia, immobilised on a fluidised sandbed, can be used very efficiently to remove nitrogenous compounds from waste and surface waters. Indeed, volumetric loading rates of 5 kg N/m^3 reactor.d were attained for an influent concentration of 500 mg NH_4^+-N/l and an upstream velocity of 53 m/h. Compared to normal activated sludge systems, the conversion rate is about ten times higher. The active biomass concentration in the reactor amounted 8.7 kg DW/m^3 reactor.

The maximum conversion rates obtained by the expanded bed reactor were 4 kg N/m^3 reactor.d for an upstream velocity of 23 m/hr. Such rates, although lower than for the fluidised bed, are still ca. 5 times those in conventional reactors. Furthermore, this reactor system is easy to start and requires only a minimum of supervision and control.

Place(s) of installation/application (including dates):

All experiments are performed at the State University of Gent, Laboratory of Microbial Ecology, Coupure L 653, B-9000 Gent, Belgium.

Director : Prof. Dr. ir. W. Verstraete

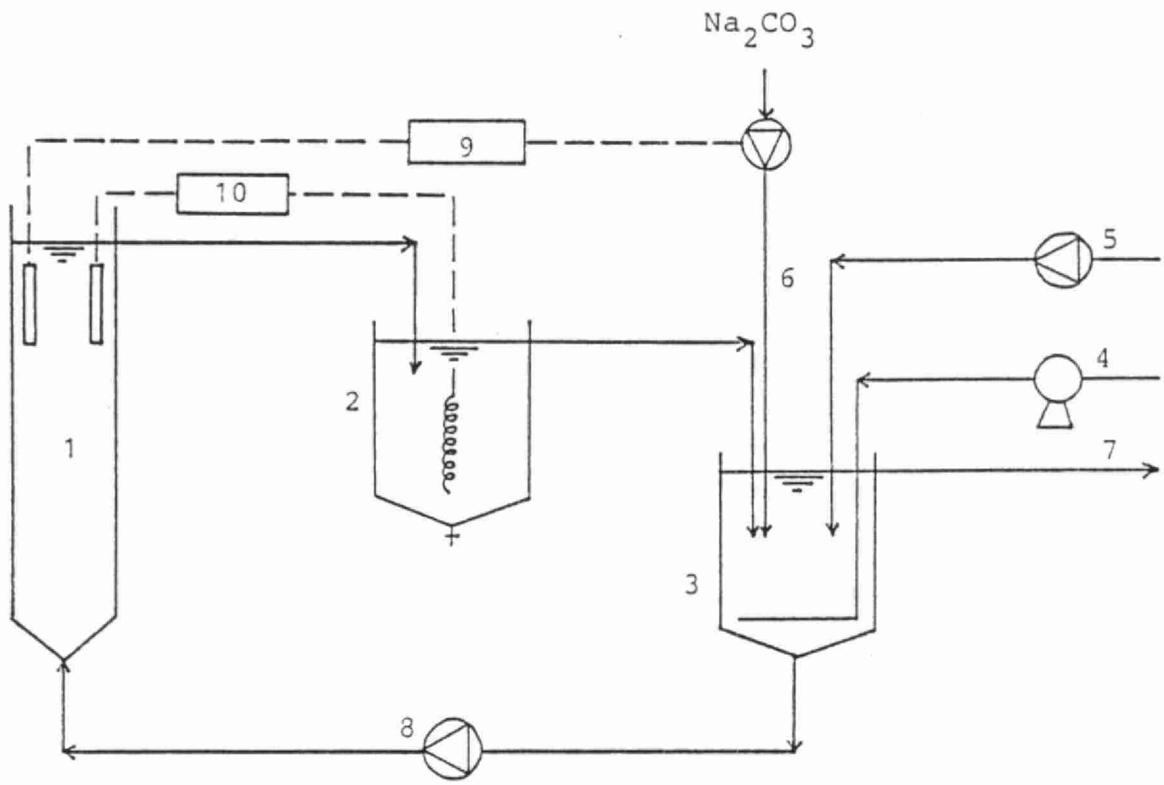
Tel. (091)23.69.61

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

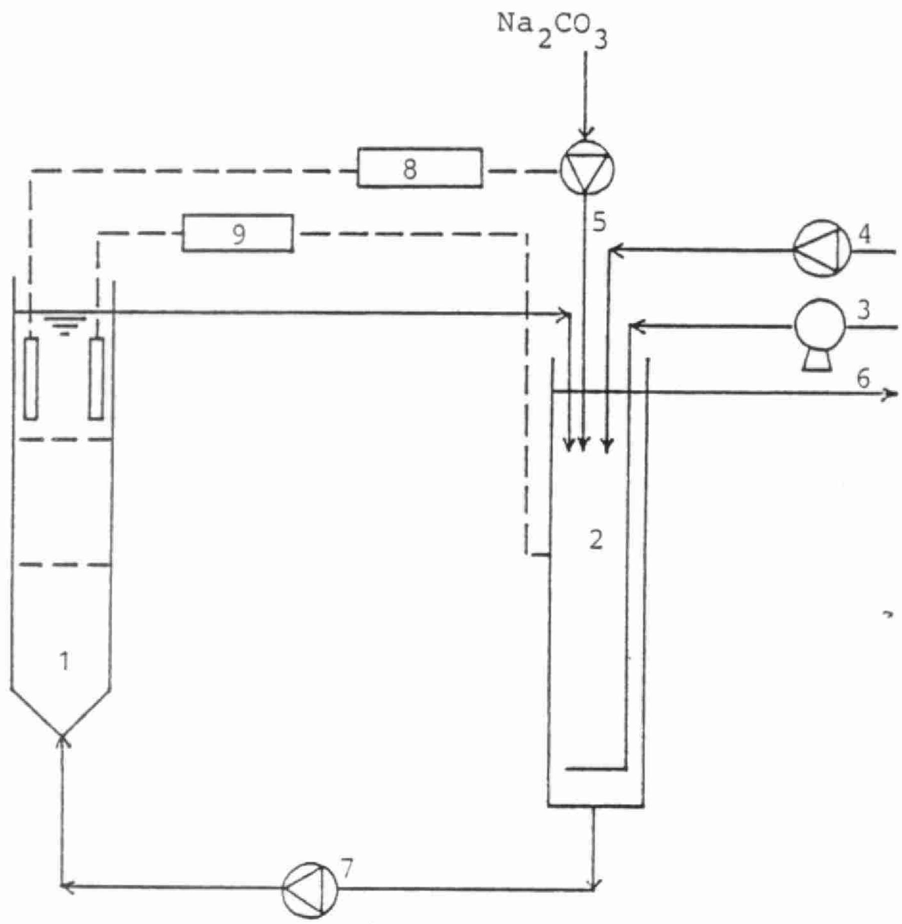
The research is supported by the S.V.W. - Studiecentrum voor Water, ir. J.G. Janssens, Scientific Coordinator, p/a A.W.W., Mechelsesteenweg 64, B-2018 Antwerpen
Tel. (03)238.78.30 - Telex 32139 AWW B - Telefax (03)237.97.66

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.



Scheme of the fluidised bed system with sand as carrier material

1. Fluidised bed reactor 2. Sandtrap 3. Mixing tank
4. Aerator 5. Influent 6. Addition of alkali 7. Effluent
8. Pump 9. pH control 10. Temperature control



Scheme of the expanded bed system with polyurethane as carrier material

1. Expanded bed reactor composed of three zones filled with polyurethane cubes 2. Mixing tank 3. Aerator 4. Influent 5. Addition of alkali 6. Effluent 7. Pump 8. pH control 9. Temperature control

USE OF FIXED BIOMASS FOR WATER AND WASTE WATER TREATMENT
37th International Conference CEBEDEAU — LIEGE, from 23-25 May 1984

ACTIVATED NITRIFICATION IN A SHALLOW FLUIDISED BED REACTOR

S. DEBOOSERE, J. GEMOETS & W. VERSTRAETE,
Lab. Microbial Ecology RUG

SUMMARY

A technique is presented to nitrify NH_4^+-N to NO_3^--N in a fluidised bed with sand as carrier material. Rather high volumetric loading rates, i.e. 5 kg N/m³r.day were hereby attained for an influent concentration of 500 mg NH_4^+-N/l. The aeration occurred with air, this in contrast with other research on fluidisation where pure oxygen is used. The optimum flow velocity and height of the reactor were estimated based on model calculations. It appears that such a reactor should in essence be shallow and wide.

INTRODUCTION

A lot of waste waters contain high concentrations of reduced nitrogen. The concentrations in the effluents of fertilizer plants, distilleries and animal rearing units reach from 1 to 5 gram per liter. High NH_4-levels arise also in industries using ion-exchangers regenerated with NH_3-gas. During anaerobic waste water treatment, the reduced nitrogen is not removed, which often results in effluent concentrations of more than 1 gram NH_4^+-N/l.

In the future, surface waters will gain more and more importance for the supply of potable water. Therefore the removal of NH_4^+-N will be necessary. Indeed, in order to achieve chlorination beyond breakpoint, 7 mg chlore is required for each mg of NH_4^+-N (1). These high amounts facilitate the formation of trihalomethanes and other undesirable chlorinated organic molecules (2). It is also known that the nitrification oxygen demand (NOD) of these nitrogen rich waste waters can severely deplete the dissolved oxygen of surface waters. The nitrification of ammonia to nitrate exerts four times as much oxygen per unit of weight as the oxidation of normal organic material. A third reason to remove NH_4^+-N from the water is the toxicity of the free NH_3 for the aquatic organisms. Indeed, already very low concentrations, i.e. 0.2 mg NH_3/l, can be harmful for fishlife (3).

Various methods exist to control ammonium-nitrogen in waste water e.g. physi-

cochemical (ion exchange and stripping), chemical (breakpoint chlorination) and biochemical (nitrification). In all of these methods, the conversion of the NH_4^+-N to NO_3^- or N_2 turns out to be quite expensive (at least 50 BF/kg N).

The technology for aerobic purification of waste water by means of a fluidised bed is not new. Yet some years ago it was shown that with sand as a carrier sludge concentrations up to 15-20 kg dry matter per m³ reactor could be reached (4, 5). By supplying aeration in the form of pure oxygen, conversions of 10 - 15 kg BOD per m³ reactor were possible (5). So far, only results of pilot reactors are known. It appears that full scale reactors still cause technical problems.

In this work, waste waters containing up to 500 mg of NH_4^+-N/l were subjected to microbiological treatment so that NH_4^+-N is converted by the bacteria to the less harmful NO_3^--N. Very high volumetric loading rates, i.e. 5 kg N/m³r.day instead of the conventional 0.1 kg N/m³r.day, were hereby attained. A fluidised bed technology was used with sand as a carrier material. Aeration occurred with air in a shallow reactor, this in contrast with other research on fluidisation where pure oxygen was used (4, 5).

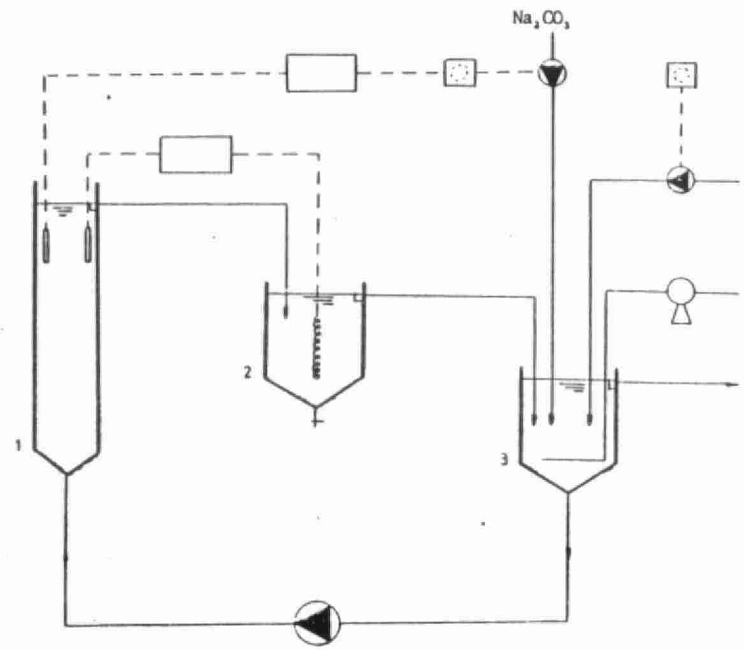
BE-26

EXPERIMENTAL

Figure 1 illustrates the basic processes of this treatment system. The water circulates in a closed circuit through the reactor (2,3 1), the sandtrap and the mixing tank. A pump with adjustable speed pumps the water upstream through the reactor (1). The sandtrap (2) prevents sand grains from damaging the pump. The mixing tank (3) has 4 functions : removal of the effluent, inlet of the influent, addition of alkali and aeration.

After a certain time the sand, overgrown with biomass, washes over in the sandtrap, due to its diminished density. The excess biomass is removed from the sand grains by a peristaltic pump which brings the sand back into the reactor. The volumetric load was increased when more than 80 % of the NH_4^+-N concentration was oxidized. An electrode controlled the pH. As soon as the pH dropped below a set value, Na_2CO_3-solution (0.2 to 0.7 N) was automatically added into to the reactor till the pH setpoint was reached again. Because the reaction velocities of <u>Nitrosomonas</u> and <u>Nitrobacter</u> are dependent on the temperature, it was necessary to keep the temperature in the reactor constant. This was achieved by a thermostat.

The reactor was filled with about 600 g of sand with a diameter of 257 to 350 µm. This means that there is a specific surface of 2600 m²/m³ reactor volume.



<u>Figure 1</u>. Scheme of the fluidised bed (FB) system with sand as carrier material

RESULTS

It took about 3 months to sufficiently colonize the sand particles with active biomass. Only after about 4 months the maximum conversion rate was reached. Nitrifying bacteria grow very slowly : the generation time of <u>Nitrosomonas</u> (conversion from NH_4^+ to NO_2^-) varies between 8 and 36 hours while for <u>Nitrobacter</u> (conversion from NO_2^- to NO_3^-) it varies from 12 to 60 hours (6). In practice, the doubling time of the nitrifying bacteria is even slower e.g. 3 to 5 days. Furthermore, the nitrifiers had to be adapted to high concentrations of NH_4^+. Thus the concentration of nitrogen was only increased when 80 % of the NH_4^+-N concentration in the influent was oxidized. Finally an influent concentration of 500 mg NH_4^+-N/l was reached. About 70 % of NH_4^+-N was oxidized at a hydraulic retention time of about 1.9 hours. Figure 2 illustrates the volumetric load (Vb) and the volumetric conversion (Vo) during the first testrun. The amounts of NH_4^+ in the influent (NH_4^+ i), in the effluent (NH_4^+ e) and of NO_2^- and NO_3^- and in the effluent are shown in Figure 3. The concentrations were measured 5 times a week till n° 57 and 3 times a week till n° 79. It was noticed that

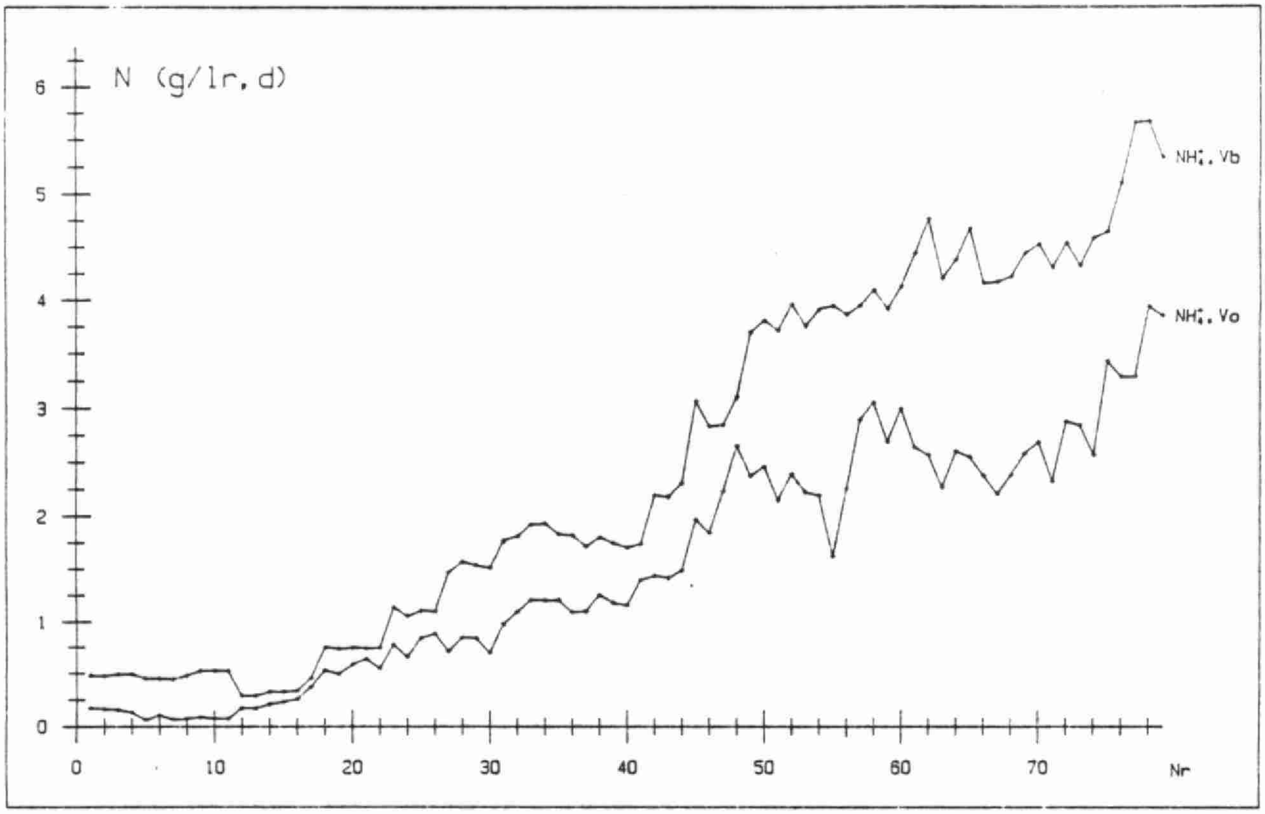


Figure 2. Volumetric loads (Vb) and volumetric conversions (Vo) of the shallow FB-system with sand

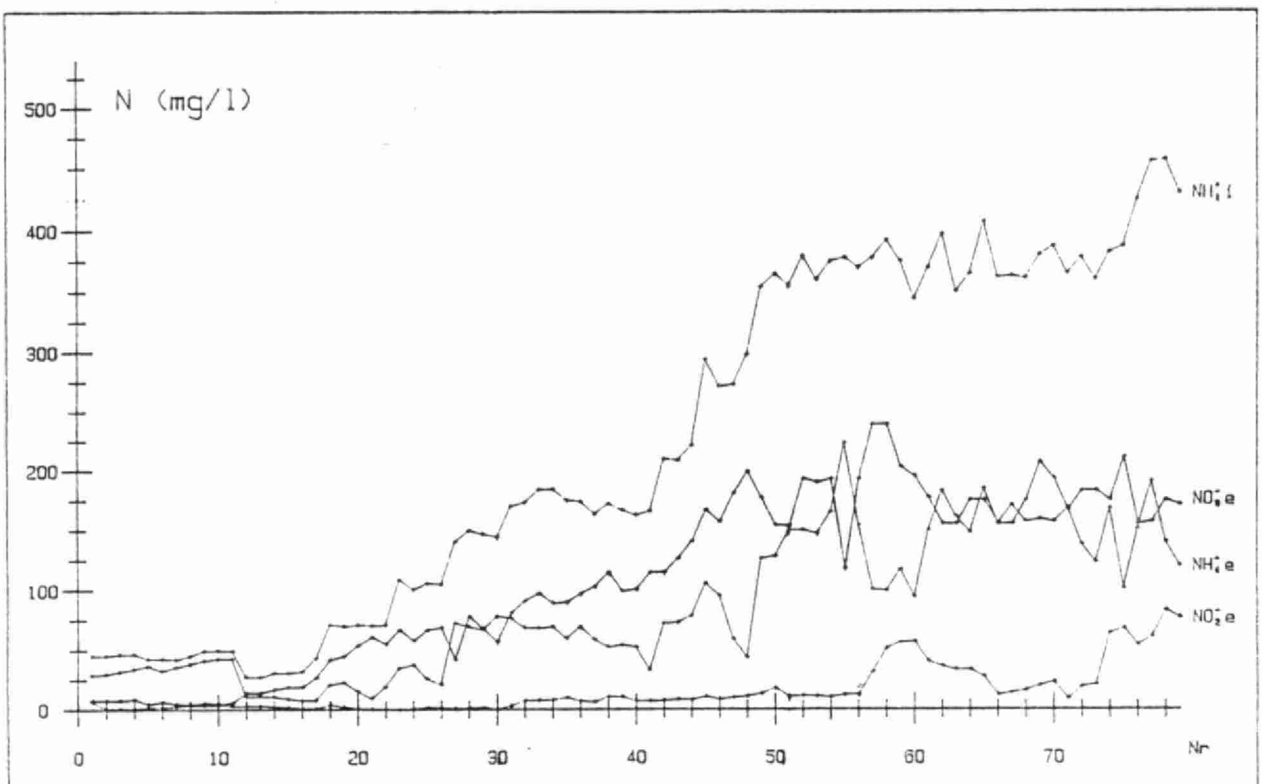


Figure 3. Nitrogen concentrations of the influent and effluent of the shallow FB-system with sand

at high influent concentrations, there was an accumulation of NO_2^-. This was probably due to the fact that in these situations, the amount of free NH_3 increased. The NH_3 has a inhibitory effect on the activity of Nitrobacter. It is known from the work of Anthonisen (7) that already 0.1 mg NH_3 can inhibit Nitrobacter. The low amounts of oxygen in the upper part of the reactor at the end of the experiment could also contribute to the accumulation of nitrite. It has been postulated that Nitrobacter is located more in the interior of the biofilm (8,14) Due to the low oxygen concentrations, the diffusion depth of oxygen is very limited. Hence, Nitrobacter is probably not capable to oxidize NO_2^- to NO_3^- when located in the inner side of the biofilm. In this case, nitrite accumulation is thus indirectly linked by the thickness of the biofilm.

In the first testrun, where the upstream velocity in the reactor was held at 40.6 m/hr, a conversion of 3.9 g NH_4^+-N/lr.d was reached.

In a second testrun, operating at 54 m/hr, an oxidation rate of 4.3 g NH_4^+-N/lr.d was possible. In a third run, operating at a velocity of 32.2 m/hr, 3.0 g NH_4^+-N/lr.d was oxidized. The results are summarized in Table I. It is important to mention that the whole system has been in operation for more than 1.5 year and this without any serious problem. It operates automatically, even the cleaning of the sand.

The biomass on the sand is very active. Particularly interesting is the observation that a large amount of protozoa and rotifers attach to the sand despite the high flow rate of the water. They probably are grazing on the bacterial biomass and thus assure that the latter has a rapid turnover and stays active.

DISCUSSION

Principles of the nitrification proces

The biochemical oxidation of ammonium - nitrogen can be brought about by autotrophic and heterotrophic microorganisms (9). The aerobic chemolithotrophic bacteria of the genera Nitrosomonas and Nitrobacter are normally responsible for the major part of the nitrification.

Two steps can be identified in the oxidation of NH_4^+ to NO_3^-; in each, oxygen has the function of electron acceptor.

$$NH_4^+ + 3/2\ O_2 \xrightarrow{Ns} NO_2^- + 2\ H^+ + H_2O \qquad \Delta G^{o\prime} = -278\ kJ \qquad (1)$$

Tabel I. Testruns at different upstreamvelocities in the fluidised bed system

Upstream velocity	Recirculation flow	Influent flow	NH_4^+-N concentration in the effluent	NH_4^+-N concentration in the effluent	NO_2^--N concentration in the effluent	Dissolved oxygen on the bottom of the reactor	Dissolved oxygen on the top of the reactor	Volumetric load of NH_4^+-N
v (m/hr)	Qr (l/hr)	Qi (l/hr)	$C_{NH_4^+-N,1}$ (mg/l)	$C_{NH_4^+-N,2}$ (mg/l)	$C_{NO_2^--N,2}$ (mg/l)	DO_3 (mg/l)	DO_4 (mg/l)	Vo (g/lr.d)
32.2	162	1.07	400	125	25	7.5	0.5	3.0
40.6	204	1.19	430	120	77	7.5	0.8	3.9
54.0	271	1.10	453	73	82	7.0	0.4	4.3

$NO_2^- + 1/2\ O_2 \Longrightarrow NO_3^- \qquad \Delta G^{\circ\prime} = -73\ kJ \quad (2)$

From equations (1) and (2) it can be derived that the stoichiometric oxygen demand for the nitrification of 1 mg NH_4^+-N to 1 mg NO_3^--N is 4.57 mg. In practice the oxygen demand is 4.33 mg per mg NH_4^+-N (10).

The nitrification process is very dependent on the pH. Nitrification is possible in the range of 5.5 to 9 (3, 6). The higher the NH_4^+-N concentration in the reactor, the more narrow this interval (7). For example, with a NH_4^+-N concentration in the reactor of 200 mg, the optimum pH is situated between 6 and 7.

The temperature is also an important factor in the nitrification process. The temperature response of both Nitrosomonas and Nitrobacter follows approximately the van 't Hoff-Arrhenius equation up to 30°C (11), e.g. if the specific growth rate at 15°C is 0.47 d^{-1} than it will be 1.21 d^{-1} at 25°C. A considerable consequence is that the efficiency can be much lower in winter than in summer, which implies longer residence times in winter.

Limitations of a fluidised bed reactor

The performance of a fluidised bed reactor is limited in two ways. On the one hand, there is a maximum amount of biomass that can be held in the reactor. On the other hand there is only a certain amount of oxygen that can be dissolved in the water. The parameter influencing both restrictions is the upstream velocity.

Limitation due to the maximum biomass concentration

The lower the upstream velocity, the more biomass is able to attach to the sand. When the velocity increases, the attrition between the particles increases, which results in a decrease of the biomass concentration. This is shown in Figure 4 (12). It illustrates also that the decrease of the biomass concentration is much greater for a thick biofilm than for a thin one.

For a given biomass concentration one can calculate a maximum conversion. Every gram of biomass can oxidize a certain amount of NH_4^+-N per unit time. Assuming that all the biomass in the reactor is active (this is fairly realistic, because the sand reactor selects for active biomass due to scouring) a new graph can be made which gives in ordinate the maximum nitrogen oxidation rate as a function of the upstream velocity (in abscissa) and this for different thicknesses of the biofilm (Figure 5). This Figure is obtained by multiplying the biomass concentration in Figure 4

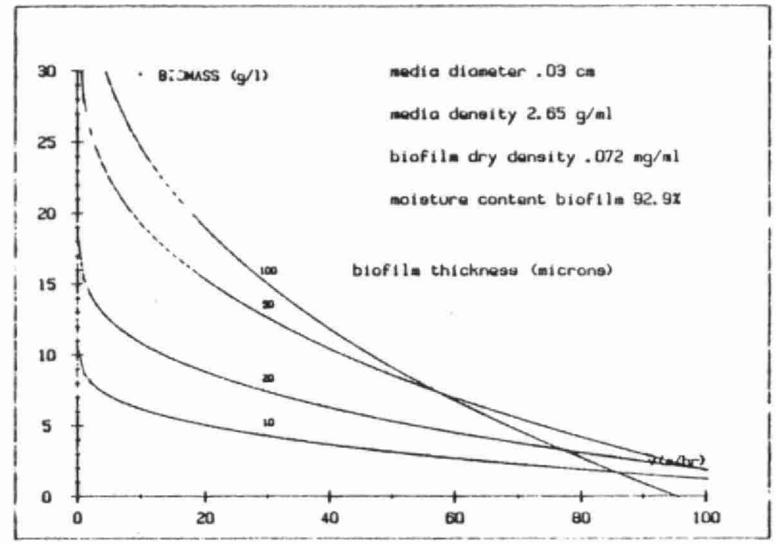


Figure 4. Influence of the superficial upstream velocity on the biomass concentration in the reactor (after Shieh et al., 1981) (12)

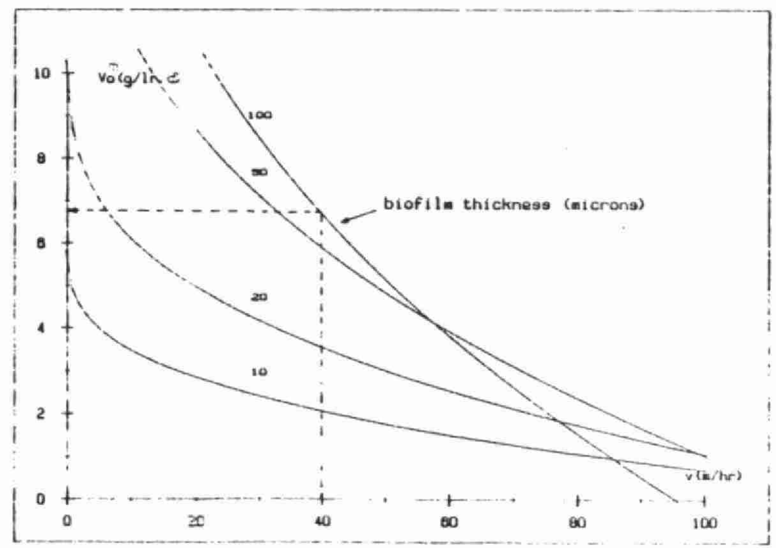


Figure 5. Maximum nitrogen oxidation V_O^m in function of the upstream velocity for different biofilmthicknesses; V_O^m = 6.9 g/l r.d at 40 m/hr

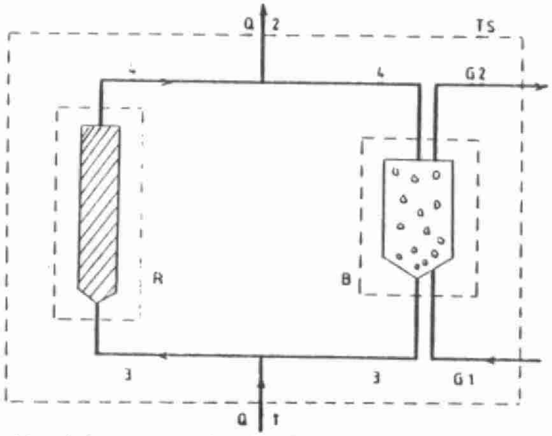


Figure 6. Mass balance zones for the whole system, the reactor and the aeration tank
R = reactorzone, B = aerationzone, TS = total system, Q = influent flow, G = aeration flow, 1 = influent stream, 2 = effluent stream, 3 - 4 = recirculation stream

Expressed in gram nitrogen per day and per liter reactor, one obtains :

$$\frac{Q \times C_{NH_4^+-N,1} \times 24}{V_R \times 1000} = \frac{Qr \times DO_3 \times 24}{4.33 \times V_R \times 1000} = V_o^m \qquad (8)$$

where V_o^m is the maximum volumetric conversion in gram per liter reactor and per day. With $Qr = A \times v$ the formula can be transformed to

$$V_o^m = \frac{24 \times DO_3 \times A}{4.33 \times 1000 \times V_R} \times v \qquad (9)$$

This is represented in Figure 7 where the maximum nitrogen oxidation is plotted as a function of the upstream velocity v and this for different values of DO_3.

The optimum upstream velocity

The combination of the two limiting factors (biomass concentration and oxygen supply) is shown in Figure 8. This figure gives the maximum conversion that can be

by the activity constant of the biomass. At pH 7 (this is the average pH of the reactor) Nitrosomonas has an activity constant of 0.8 g NH_4^+-N/g DM.day and Nitrobacter oxidizes 1.8 g NO_2^--N/g DM.day (13). For a total conversion to NO_3^-, 1/0.8 + 1/1.8 = 1.805 g DM biomass is needed to oxidize 1 g NH_4^+-N. Hence, the total activity constant of the nitryfying biomass is 0.544 g N/g DM.d.

Limitation due to the maximum oxygen supply

The higher the upstream velocity and by this also the recirculation flow, the more oxygen can be supplied. Using the mass balance of the system, a relation can be found between the maximum nitrogen conversion and the aeration capacity of the aeration tank. Therefore, the recirculation flow reactor-aeration tank has to be analysed as a system on its own, and for its different components (Figure 6). This gives the following balances :

- the nitrogen balance for the whole system $Q\,(C_{N,1} - C_{N,2}) + r_N \times V_R = 0$ (3)
- the oxygen balance for the reactor $Qr\,(DO_3 - DO_4) + r_{O_2} \times V_R = 0$ (4)

with C : concentration of ammonium (mg/l)
DO : dissolved oxygen (mg/l)
r : reaction velocity per volume-unit (mg/l.hr)
V_R : volume of the reactor (l)
Qr : recirculation flow (l/hr)

Combining (3) and (4) gives :

$$\frac{Q\,(C_{N,1} - C_{N,2})}{Qr\,(DO_3 - DO_4)} = \frac{r_N \times V_R}{r_{O_2} \times V_R} \qquad (5)$$

These equations are valid for the formation of NO_2^- and NO_3^- as well. For a total conversion to NO_3^-, this expression becomes :

$$Q \times 4.33 \times (C_{NH_4^+-N,1} - C_{NH_4^+-N,2}) = Qr\,(DO_3 - DO_4) \qquad (6)$$

(with $\frac{r_{O_2}}{r_N} = 4.33$: the conversion of 1 mg NH_4^+-N to 1 mg NO_3^--N needs 4.33 mg oxygen).
In this equation $Q\,(C_{NH_4^+-N,1} - C_{NH_4^+-N,2})$ is the amount of nitrogen that is nitrified in one hour (mg/hr). Consequently, the latter multiplied by 4.33 represents the oxygen consumption for this conversion. The right hand side of this equation $Qr(DO_3 - DO_4)$ is the amount of oxygen that is supplied (mg/hr). The maximum nitrogen oxidation (with a total conversion of ammonium to nitrate) can be calculated assuming that in the upper part of the reactor all the oxygen is consumed ($DO_4 = 0$) and that there is no more NH_4^+-N in the effluent ($C_{NH_4^+-N,2} = 0$). This yields the following equation :

$$Q \times C_{NH_4^+,1} = \frac{Qr \times DO_3}{4.33} \qquad (7)$$

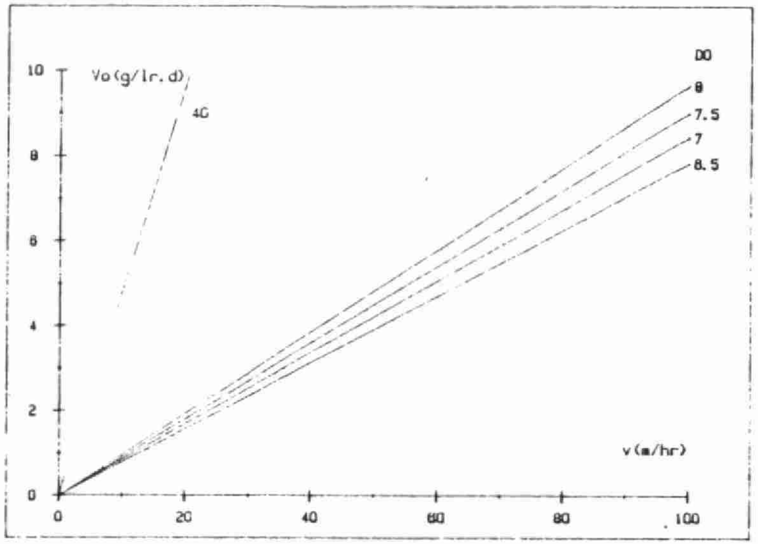


Figure 7. Maximum nitrogen oxidation V_o^m for the used reactor in function of the upstream velocity, at different values of DO_3

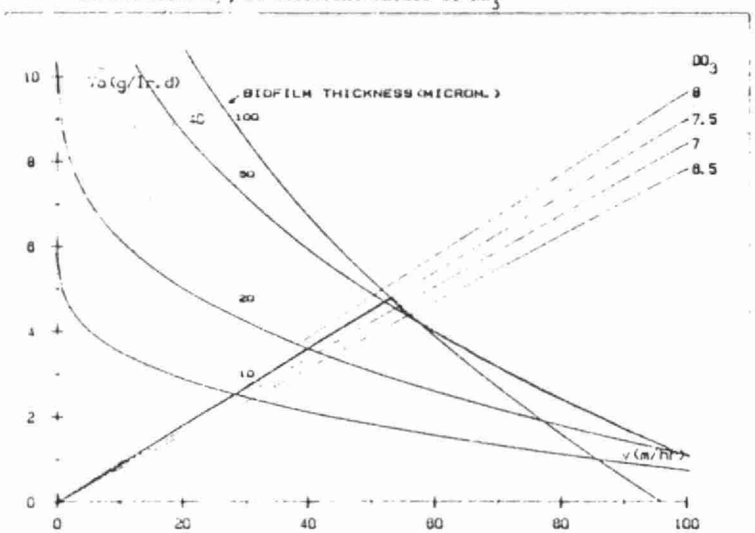


Figure 8. Maximum oxidation capacity of the FB-system in function of the upstream velocity and biofilm thickness. The heavy line shows the limitation of V_o^m based on a maximum biomass concentration and on DO_3 = 7.5 mg/l

reached as a function of the upstream velocity for different values of DO_3 and for variable thickness of the biofilm. The intersection between the straight line and the curve at the highest distance from the origin, indicates the optimum upstream velocity. For example, a DO_3 = 7.5 mg/l corresponds with an optimum upstream velocity of 53 m/hr, and a maximum conversion of 4.8 g NH_4^+-N/lr.d. It can also be derived from this figure that the higher the amount of dissolved oxygen, the lower the upstream velocity and therefore the lower the recirculation flow.

The optimum height

Suppose a cylindrical reactor. In this case the formula (9) can be transformed (with $\frac{A}{V_R} = \frac{1}{H}$) to :

$$H = \frac{24 \times DO_3}{4.33 \times 1000 \times V_o^m} \times v \qquad (10)$$

So V_o^m can be expressed as a function of H and this for different upstream velocities. To each upstream velocity, a maximum conversion (V_o^m) corresponds, based on the maximum biomass concentrations (Figure 5). This is illustrated in Figure 9. Quite remarkable is the fact that the optimum height of the reactor, at a velocity of 40 m/hr, is only 24 cm. The height of the reactor used was 45 cm. As mentioned before, at a velocity of 40m/hr a conversion of 3,9 g N/lr.d was reached. If the height was optimized to 24 cm by using a wider reactor, then the conversion rate could increase to 6.9 g N/lr.d.

Remarks

The computed values have to be considered as indicative. In Figure 4 e.g., an average biofilm thickness is used. In reality, the biofilm thickness will increase from the bottom to the top of the reactor. Furthermore the maximum biomass concentration was calculated with a given density of the biofilm, and this density can differ a lot depending on the origin of the waste water. The activity constants of Srinatch et al. (13) are the third factor which must be interpreted with care. Indeed, the activity of the nitrifying bacteria strongly depends on the environmental conditions and these values are therefore approximative. Nevertheless the good correspondence between the experimental results and the theory, especially with regard to the oxygen limitation, indicates that the overall approach is quite valid.

It is also clear that the height calculated here is the minimum useful height. For practical reasons, such as washout, short-circuiting currents, the real height will be somewhat larger.

All data relate to an ambient temperature of 20°C. Other temperatures will give

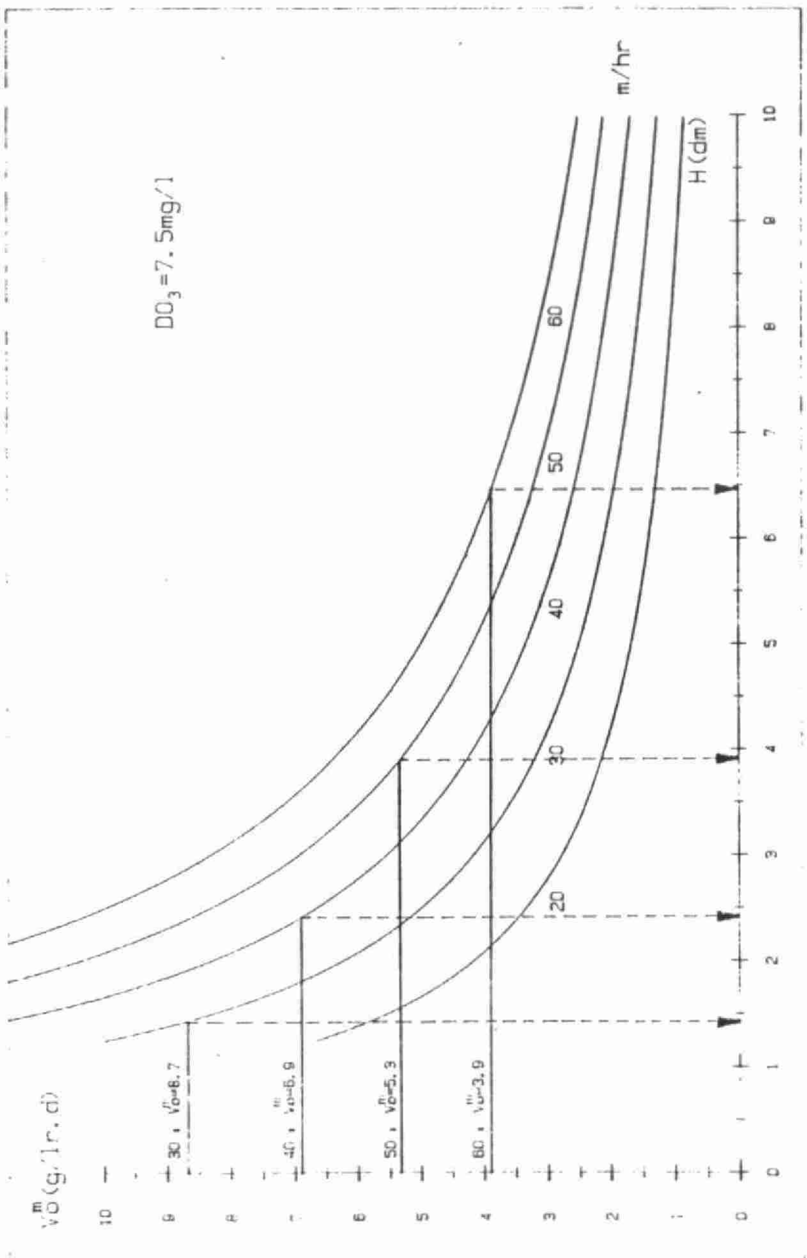


Figure 9. Optimum height of the reactor at different upstream velocities and at DO_3 = 7.5 mg/l

other optimum values. In practice, once the height of the reactor is fixed, the optimum velocity will be determined using graphs similar to those in Figure 8.

CONCLUSION

The fluidised sandbed reactor provides a good alternative to nitrify the NH_4^+-N of waste waters. Due to the high conversion rates (up to ten times higher than normal active sludge systems) the reactor will be very small. Because the biomass is in a concentrated form attached to the sand, no secondary clarifiers are necessary. However a system is needed to detach the surplus sludge from the sand. The use of air requires a high recirculation of the water, but this method seems to be a better approach than aerating with pure oxygen. From the Figures 8 and 9, the optimum velocity and optimum height of the reactor can be calculated. This reactor will in essence be shallow and wide. Further research is necessary to explore the practical implications of these laboratory studies.

ACKNOWLEDGEMENT

This present work was carried out in the laboratory of Microbial Ecology of the State University of Ghent. We like to thank the "Studiesyndicaat voor Water (S.V.W.)" who financed this research and its workgroup "Treatment of nitrogen rich effluents" who guided this investigation.

A detailed study of this work is available entitled "Geactiveerde nitrificatie in een gefluïdiseerd en geëxpandeerd bed" (14).

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PROJECT DESCRIPTION

Project Title: **S.V.W. Project A/022:**

Biological Denitrification of Drinking Water by means of Hydrogen-Oxidizing Bacteria in a Polyurethane Carrier Reactor

Contact (name of person, organization, address, telephone):

Prof. Dr. ir. W. Verstraete - Director
Ir. J. Liessens - Project Leader
Laboratory of Microbial Ecology, State University of Gent,
Coupure L 653, B-9000 Gent, Belgium

Tel. (091)23.69.61

Project Description (Please attach a schematic diagram if appropriate):

The presence of nitrates in groundwater and surface water represents one of the major risks for public health. Indeed, conventional methods for the production of drinking water do not remove nitrate. Hence, there is a strong demand for new methods to selectively remove nitrate from drinking water.

A new reactor type has been developed for microbiological nitrate removal with H_2 as the reductant. The reactor is equipped with polyurethane lamellae as the support matrix for the autotrophic H_2 oxidizing microorganisms. Hydrogen is diffused in a downflow column in countercurrent with the nitrate loaded water. To improve the efficiency of gas transfer, the residual H_2 in the gasphase is recycled. The partially denitrified water subsequently enters an upflow column, where in the lower part, the residual dissolved H_2 is exhausted and the remaining nitrate and nitrite reduced. In the upper part, the water is reaerated and through nitrifying bacteria purified from intermediary nitrogenous compounds. The whole system is operated at a pressure of 1 bar.

This process is attractive in the treatment of drinking water because nitrate is selectively eliminated. Hydrogen is completely harmless to potable water and in contrast to substrates such as methanol or ethanol, no further steps are needed to remove residual organics.

A pilot-plant (50 m^3/d) is built in a water production centre where drinking water is produced out of surface water. The efficiency is compared with an operational fluidized bed and fixed bed reactor, both with methanol as the reductant.

Operating and cost data (including data on efficiency, results, etc.):

Laboratory studies have confirmed the technological and economical feasibility of this process. Autotrophic reaction rates are relatively low compared to heterotrophic conversions. Therefore, the lamellar polyurethane matrixes characterized by a high specific area (> 1000 m^2/m^3) provide high biomass densities of more than 10 kg VSS/m^3 reactor. The production of excess biomass is very low (0.3 kg DW/kg NO_3^--N). The specific NO_3^--N removal rate of the hydrogenotrophic biomass amounted 0.25 kg NO_3^--N/kg VSS.d (20 °C). Maximum denitrification rates of 1.75 kg NO_3^--N/m^3 total reactor.d were achieved at 20 °C for water containing 15 mg NO_3^--N/l. By recycling the gasphase, the efficiency of H_2 transfer is increased up to 75 %. This reduces the operating costs which amounted 2 BF/m^3 of denitrified water.

Place(s) of installation/application (including dates):

Laboratory experiments are performed at the State University of Gent. The pilot plant will be realised at the water production centre "De Blankaart", Woumen, West-Vlaanderen, in cooperation with the V.M.W.-Vlaamse Maatschappij voor Watervoorziening. The plant will be operational in May '88.

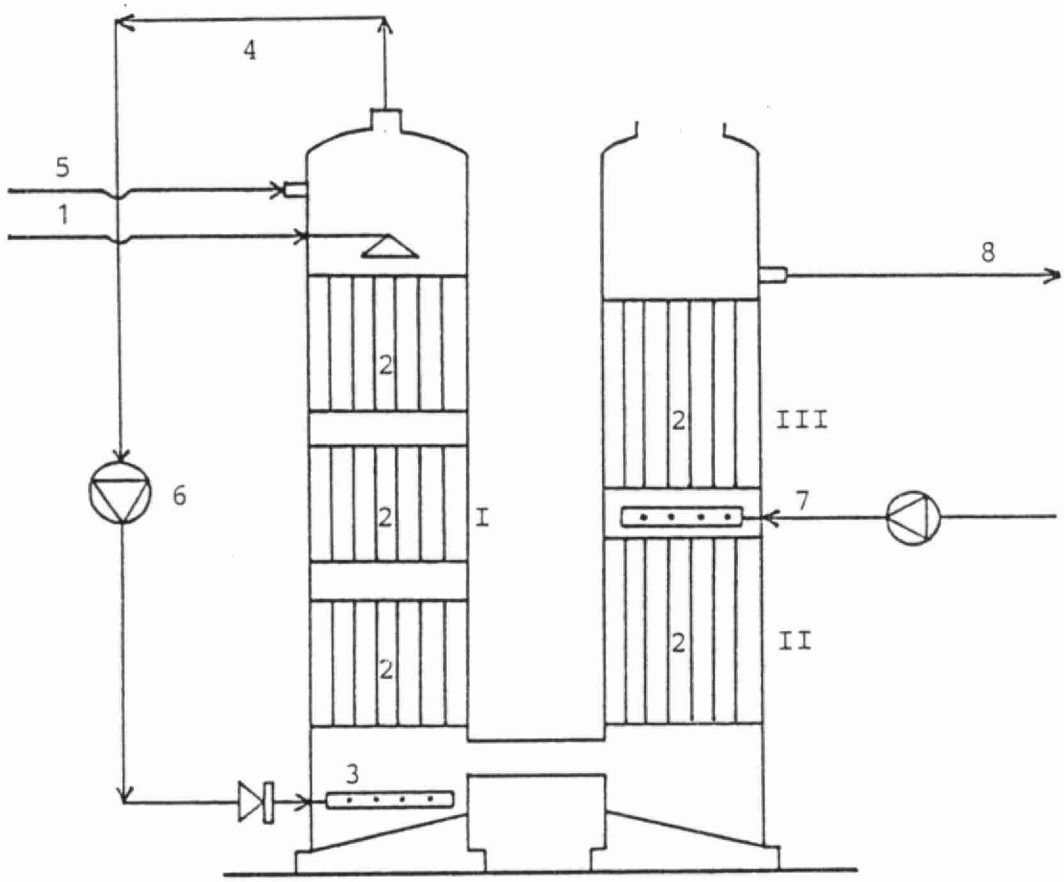
Patent staus, if applicable:

United States Patent N° 4,696,747 of Sep. 29, 1987
"Process for the Elimination of Nitrates by means of a Microbiological Conversion in the Presence of Hydrogen Gas".

Other information (e.g., funding source, cooperating agencies, etc.):

The research is supported by the S.V.W. - Studiecentrum voor Water, Ir. J.G. Janssens - Scientific Coordinator, p/a A.W.W., Mechelsesteenweg 64, B-2018 Antwerpen
Tel. (03)238.78.30 - Telex 32139 AWW B - Telefax (03)237.97.66

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.



Scheme of the denitrification reactor

I. Denitrification reactor   II. Post-denitrification reactor
III. Nitrification reactor   1. Nitrate loaded water   2. Polyurethane lamellae   3. Hydrogen diffusor   4. Gas recirculation   5. External hydrogen dosage   6. Gas recirculation pump   7. Air diffusor
8. Denitrified aerated water

Wat. Supply, Vol. 6, Brussels, pp. 181–192, 1988.
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NITRATE REMOVAL FROM DRINKING WATER BY MEANS OF HYDROGENOTROPHIC DENITRIFIERS IN A POLYURETHANE CARRIER REACTOR

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ABSTRACT

Hydrogen can be used as non-polluting and non-toxic reductant to remove nitrate from ground and surface water in the process of drinking water production. Denitrification with H_2 gas has been studied in a reactor containing microbial biomass fixed on polyurethane matrixes. Nitrate loaded water enters at the top of a downflow column and moves through the reactor in countercurrent with the upwards rising H_2 gas. The water subsequently enters an upflow column. In the lower part of the second column, the residual dissolved H_2 is exhausted and the remaining NO_3^--N and NO_2^--N reduced. In the upper part of the second column the water is reaerated and through nitrifying bacteria attached to the carrier matrix, purified from intermediary products as NO_2^--N. Conditions have been optimized for nitrate removal, H_2 transfer and biomass accumulation. For water containing 15 mg NO_3^--N/l removal rates of 0.5 g N/l total reactor.day are reached at 20°C. The efficiency of H_2 transfer amounts to 50 - 55 %. This denitrification system qualifies as a safe and extensive method to remove nitrate from drinking water.

KEYWORDS

Lithotrophic denitrification; denitrification; hydrogen; gas recirculation; polyurethane; drinking water; nitrification.

INTRODUCTION

During the last decade, the presence of nitrate in ground and surface waters has become of increasing concern. A correlation has been shown between intensively cultured land and high nitrate content in the sources of water supply (De Brabander and Labeau, 1986; Timmermans, 1983). Nitrate loaded water used for drinking water production can cause health problems (Comly, 1945; Fraser and co-workers, 1980; Jensen, 1982). The World Health Organisation (W.H.O.) and the European Economical Community (E.E.C.) have set guidelines and limits for the nitrate and nitrite content in drinking water (Table 1) (Germonpré, 1985).

TABLE 1 Standards for Nitrate and Nitrite Content in Drinking Water as listed by the W.H.O. and the E.E.C.

		Nitrate (mg NO_3^--N/l) GL*	MAC**	Nitrite (mg NO_2^--N/l) GL*	MAC**
W.H.O.	(1984)	11.30	-	-	-
E.E.C.	(1980)	5.65	11.30	-	0.03

* GL = Guideline
** MAC = Maximum Acceptable Concentration

Conventional methods for the production of drinking water do not remove nitrate. Hence, in recent years methods have been sought to remove nitrate from ground and surface waters. Physical and chemical methods for nitrate removal, such as ion exchange, reverse osmosis and electrodialysis, have the disadvantage of being not selective for the nitrate ion. This gives problems in case the water is rich in other ions, e.g. sulphate. They furthermore produce residual nitrate-rich concentrates (S.WW-rapport, 1984; Van der Hoek, 1984). Biological denitrification is based on the capacity of certain microorganisms to reduce nitrate to dinitrogen gas. Depending on the use of an organic or inorganic source of reducing equivalents, one distinguishes organotrophic, resp. lithotrophic denitrification. Methanol is the most commonly quoted carbon source.

The biological process examined in this study is based on lithotrophic denitrification. Inorganic HCO_3^--ions and carbonic acid dissolved in the water are used as C-source and H_2 gas acts as the reducing agent. Under conditions where the concentration of dissolved oxygen is low or zero, nitrate acts as the electron acceptor. The chemical reactions of the nitrate reduction can be schematized as follows :

$$2\ NO_3^- + 2\ H_2 \longrightarrow 2\ NO_2^- + 2\ H_2O \quad \text{(eq. 1)}$$
$$2\ NO_2^- + 3\ H_2 + 2\ H^+ \longrightarrow N_2 + 4\ H_2O \quad \text{(eq. 2)}$$
$$2\ NO_3^- + 5\ H_2 + 2\ H^+ \longrightarrow N_2 + 6\ H_2O \quad \text{(eq. 3)}$$

Several reactor configurations, such as suspended bed, fixed bed and fluidized bed can be applied for biological denitrification (Gauntlett, 1981). In this study, a fixed bed reactor with polyurethane (PU) sponges as carrier material for the microbial biomass was used. The high specific area and high porosity of the sponges permit a good biomass growth and adherence. The sponges are fabricated of reticulated polyurethane foams. The two main compounds of these foams are polyisocyanate and polyol. Depending on the sort of polyol - polyesterpolyol or polyetherpolyol - one distinguishes polyesterpolyurethane (PU-S) resp. polyetherpolyurethane (PU-T). The PU-T sponges are mostly used in water treatment. The pore size of these sponges can be regulated between 10 - 100 pores per inch. The density varies between 26 - 32 kg/m³ and the porosity fluctuates around 97 % (Recticel, 1986).

MATERIALS AND METHODS

Reactor System 1

The experimental reactor is composed of two plexiglass tubes with a total height of 2 m and an internal diameter of 44 mm (Fig. 1). The reactor consists of a downflow and an upflow column. The columns are interconnected and filled with polyurethane sponges (5) which allow accumulation of the microbial biomass. The gas is introduced at the bottom of the downflow column (= denitrification reactor = DN1 (4)) at a rate of 0.13 l/cm² cross section.min or 2 l/min unless otherwise indicated. The mean diameter of the gas-bubbles in the DN1 is 5 mm. Tap water (1) and a concentrated sodium nitrate solution (2) are continuously fed at the top of the DN1 by means of a peristaltic metering pump (3) (Verder). The denitrifying microorganisms attached in the carrier matrix transform nitrate to dinitrogen gas using the upwards diffusing H_2 gas. The non-consumed H_2 and the produced N_2 are recycled (12) through a gascolumn (13) by means of a gastight pump (Verder) back to the DN1. In the lower part of the upflow column (= post-denitrification reactor = DN2 (6)), the remaining nitrate and/or nitrite nitrogen are further removed microbiologically, thus exhausting the residual dissolved hydrogen. Finally, the water enters the upper part (= nitrification reactor (7)), where it is reaerated to assure a minimum dissolved oxygen level of 4 mg/l, which allows nitrifying bacteria to remove hazardous residual nitrogeneous intermediates such as nitrite.

At the start of the tests, the gasphase in the closed gascircuit is flushed till 100 % H_2 is attained. The gasphase is in balance with the atmospheric pressure. According to the overall denitrification reaction (eq. 3), the reduction of 28 g NO_3^--N consumes 5 moles of H_2 and produces 1 mole of N_2. This leads to a decrease of the total gasvolume. Moreover, N_2 dissolves better in water (csN_2 = 17.4 mg /l at 20°C) than H_2 (csH_2 = 1.5 mg/l at 20°C). As a consequence denitrification creates an under-pressure. To prevent this, the H_2 consumed is constantly refilled from the gasreservoir (16).

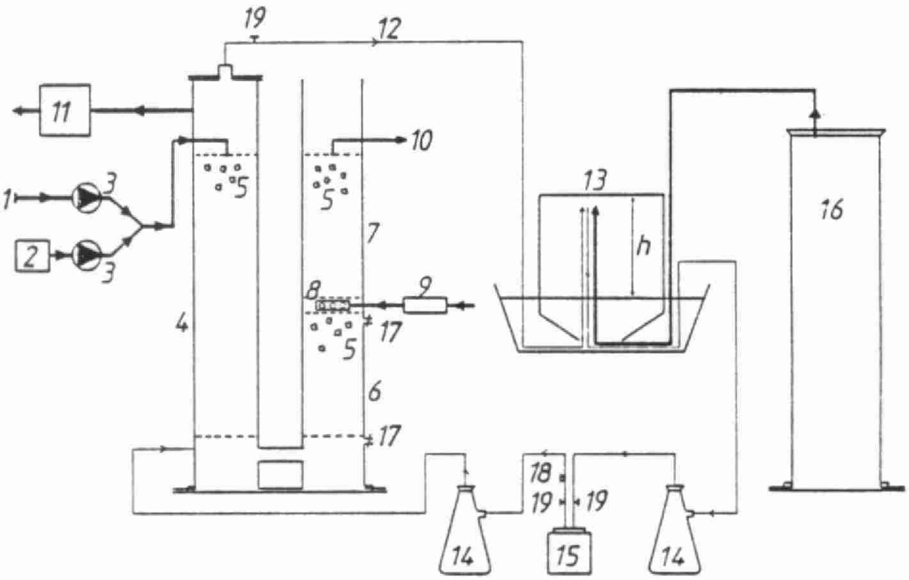

Fig. 1. Denitrification reactor with gas recirculation
1. Tap water 2. Sodium nitrate solution 3. Peristaltic metering pump 4. DN1 (=denitrification reactor) 5. Biomass carrier matrixes 6. DN2 (= post-denitrification reactor) 7. Nitrification reactor 8. Air diffuser 9. Airpump 10. Denitrified aerated water 11. Water seal 12. Gas recirculation 13. Gascolumn 14. Buffertank 15. Gaspump 16. Gasreservoir 17. Sampling point 18. Gas sampling point 19. Flushing point

The total reactor (= DN1 + DN2 + Nitrification reactor) has a volume of 4.26 l

The reactor contained 3 different types of PU sponges, i.e. PU-T10, PU-T30 and PU-T45. The characteristics of these sponges are described in Table 2. The PU was provided in the form of cubes with 1 cm rib.

TABLE 2 Characteristics of the PU Sponges in the Reactor (Recticel, 1986)

	T10	T30	T45
Pores per inch	10	30	45
Pore diameter (mm)	2.19	0.97	0.56
Wire thickness (µm)	254	140	65
Wire per cm^3 sponges (cm/cm^3)	61	309	1008
Specific area (m^2/m^3)	488	1375	2057

The bottom layer of the DN1 consisted of 140 cubes PU-T10. The upper part was composed of 307 cubes PU-T30 and 396 cubes PU-T45. The DN2 contained 12 cubes PU-T10 at the bottom and resp. 32 and 295 cubes PU-T30 and PU-T45 in the upper part. Finally, the nitrification reactor was filled with 478 cubes PU-T45. As a whole, a 40 % of the reactor volume was occupied by polyurethane matrix. The surface at the outside of the cubes was 242 m^2/m^3 reactor, the total surface (outside + inside) of the cubes amounted to 714 m^2/m^3 reactor.
The characteristics of the incoming water are summarized in Table 3.

TABLE 3 Characteristics of the Incoming Water of the Denitrification Reactor System 1

pH	-	7.4 - 7.6
Dissolved oxygen (DO)	mg/l	8 - 11
Temperature	°C	12 - 20
Total hardness	°F	38 - 47
Ca^{2+}	mg/l	127 - 150
Total alkalinity (TAM)	meq/l	4.8 - 5
Total dissolved salts	mg/l	400 - 420
NO_3^--N	mg/l	50
NO_2^--N	mg/l	0
NH_4^+-N	mg/l	0

To start up the reactor, the water entering was enriched with minerals i.e. phosphorous, magnesium and iron to provide sufficient nutrients for the establishment of the denitrifying biomass. The water was also seeded with a culture of Alcaligenes eutrophus ATCC 17697, a denitrifying microorganism. The nitrification reactor was seeded with an enrichment of nitrifying bacteria obtained from soil and surface water. During the experiments 100 ml soil extract, obtained by filtering 10 g of soil in 1 l of tap water, was daily added to the influent as a source of minerals for the microorganisms. The excess sludge in the DN1 was weekly removed by turbulent air injection (10 l/min or 0.66 l/cm^2 cross section.min) during 20 minutes and subsequent drainage of the biomass detached.

Reactor System 2

The same reactor configuration, as shown in Fig. 1, was used. However, the reactor was equipped with strips instead of cubes of PU sponges. The properties of the used strips PU-T30 are similar to these of the cubes PU-T30, mentioned in Table 2. The carrier matrix occupied ca. 44 % of the volume. The surface at the outside of the strips amounted to 230 m^2/m^3 reactor, the total surface (outside + inside) of the strips was about 600 m^2/m^3 reactor.
For a first series of experiments, hard water as characterized in Table 3 was used as influent, except for the NO_3^--N concentration which amounted to 15 instead of 50 mg N/l. For a second series of tests, soft water with the characteristics listed in Table 4 has been used. The reactor was started and operated in the same way as mentioned before for reactor system 1, only that Na_2HPO_4 (1.1 mg P/l) was added as an extra P-source instead of the daily addition of 100 ml soil extract.

TABLE 4 Characteristics of the Soft Water as Influent for the Denitrification Reactor System 2

pH	-	6.1 - 6.4
Dissolved oxygen (DO)	mg/l	8 - 11
Temperature	°C	12 - 20
Total hardness	°F	18 - 22
Ca^{2+}	mg/l	58 - 66
Total alkalinity (TAM)	meq/l	1.6 - 1.7
Total dissolved salts	mg/l	400 - 420
NO_3^--N	mg/l	15
NO_2^--N	mg/l	0
NH_4^+-N	mg/l	0

Analytical Methods

The pH was measured potentiometrically with a RADIOMETER pHM32. The nitrate concentration was determined with a specific ORION nitrate electrode with $KAl(SO_4)_2$ as background electrolyte. The nitrite concentration was determined by the colorimetric method of Montgomery and Dymock (1961). The dissolved oxygen (DO) was measured with an oxygen electrode (BECKMAN Monitor System II). Gas analyses were performed on an Intersmat IGC-120 MB chromatograph equipped with a Hewlett-Packard 3390A Integrator and a dual column arrangement of Porapack Q (80 - 100 mesh) and a molecular sieve 5 Å to separate H_2 from N_2.

To determine the dry weight (DW) of the biomass in the PU sponges, a known volume of the colonized sponges was removed from the reactor and dried to constant weight at 110°C. Taking into account the total amount of sponges in the reactor and their uncolonized dry weight, the biomass concentration per unit of reactor volume was thus calculated. The Sludge Volume Index (SVI) was determined as the volume (ml) occupied by 1 g of sludge after 30 min of sedimentation.

The denitrifying biomass was microscopically examined using a Polyvar (Reichert-Jung) microscope equipped with Interferention Phase Contrast. The bacteriological quality of the drinking water produced was regularly determined on specific media. Total colony forming units (CFU) were determined after a growth period of 3 days at 37°C on Nutrient agar (Oxoid). Azide dextrose broth (Difco) was used to grow fecal streptococci for 3 days at 37°C. Coliforms and fecal coliforms were determined in MacConkey broth (Difco) after incubation at 37°C (3 days) and 43°C (1 day) respectively.

RESULTS

Process Performance of Reactor System 1

First, the reactor was started and operated without recirculation of the non-consumed H_2 gas. At the bottom of the DN1, pure hydrogen was gradually bleeded from a gasreservoir at constant pressure and constant flow. The rate of gasinjection amounted to 8.9 l H_2/l total reactor (lr tot).d (where total reactor = DN1 + DN2 + Nitrification reactor). Tap water (characteristics mentioned in Table 3) containing 50 mg N/l entered the DN1. Steady state conditions were reached about 5 weeks after imposing the process conditions. At a volumetric loading rate of 0.5 g N/lr tot.d, the efficiency of nitrate removal amounted to 80 - 100 % considering a total retention time of 144 min. The efficiency of H_2 transfer, calculated from the experimental data and the overall denitrification reaction (eq. 3), was found to vary from 15 to 20 %. Table 5 shows the composition of the water for the different reactor zones.

TABLE 5 Composition of the Water for the Different Reactor Zones at Steady State Conditions in Reactor System 1 without Gas Recirculation

		Influent	Effluent DN1	Effluent DN2	Effluent total reactor
NO_3^--N	(mg/l)	50	15	0 - 5	0 - 10
NO_2^--N	(mg/l)	0	5 - 10	0 - 5	0
pH	(-)	7.4 - 7.6	8.5 - 8.9	8.9 - 9.4	8.0 - 8.5
DO	(mg/l)	8 - 11	1.0	1.0	8.0

The denitrifying biomass attached to the densely packed PU support matrix amounted to 20 g DW/l reactor for the DN1. All microbiological analyses of the effluent were negative for total coliforms, fecal coliforms and fecal streptococci. The total number of CFU ranged from 10^3 - 10^4/ml final effluent.

In a separate experiment, the reactor was operated under the same conditions but the H_2 dosage was gradually decreased to observe the effect on the overall removal rate. As the H_2 supply was lowered, a strong accumulation of NO_3^--N was observed in the effluents of DN1 and DN2, yet the NO_2^--N was totally converted to NO_3^--N during the nitrification phase. The decrease in efficiency of denitrification at the lower rates of H_2 reflect the importance of the diffusion of the reductant into the biomass layer (Fig. 2).

In a second series of tests, the gasphase was constantly recirculated through the reactor. At the onset, the gasphase was flushed till 100 % H_2 was attained. The operating conditions for the different reactor zones during this experiment are summarized in Table 6. The total liquid flow amounted 20 l/d for an influent containing 50 mg N/l. Daily 10 l H_2 were applied from the gasreservoir to maintain a total pressure of 101.3 kPa in the gascircuit.
Figure 3 shows the evolution of the nitrate content for the different reactor zones. From day 2 till day 6 all nitrate was removed in DN1 and DN2, but from day 4 on a slow increase of nitrite was observed in the effluent of DN1 and DN2 (Fig. 4). During these 6 days, the percentage H_2 in the gasphase decreased from 100 to 85 - 82 %.
From day 7 on, the nitrate removal dropped very rapidly to 70 % in the DN1 and to 60 % in the total reactor. At the same time, nitrite accumulated in DN1 and DN2 (Fig. 4). Yet, the latter was completely reconverted to nitrate in the subsequent nitrification reactor. The percentage H_2 in the gasphase decreased to 75 - 80 % and stabilized from day 7 onwards. Till day 6, the efficiency of the nitrate removal was 100 % and the efficiency of H_2 transfer fluctuated around 38 - 40 %. From day 7 onwards, these values decreased to 60 % and 25 % resp. During the whole testrun, N_2O was not detected in the gasphase. Figures 5 and 6 show the efficiency of nitrate removal and H_2 gift for respectively DN1 and the total reactor.
In the upper part of the DN1, facultative anaerobic microorganisms develop and consume the DO in the effluent as electron acceptor. When the DO-value drops below 1 mg/l, denitrification starts. After nitrification, a well aerated water is produced with a DO level of 7 - 8 mg/l. Due to denitrification in the DN1 and DN2, the pH increases up to 8.4 - 8.9. Nitrification subsequently decreases the pH to 8.0 - 8.2.

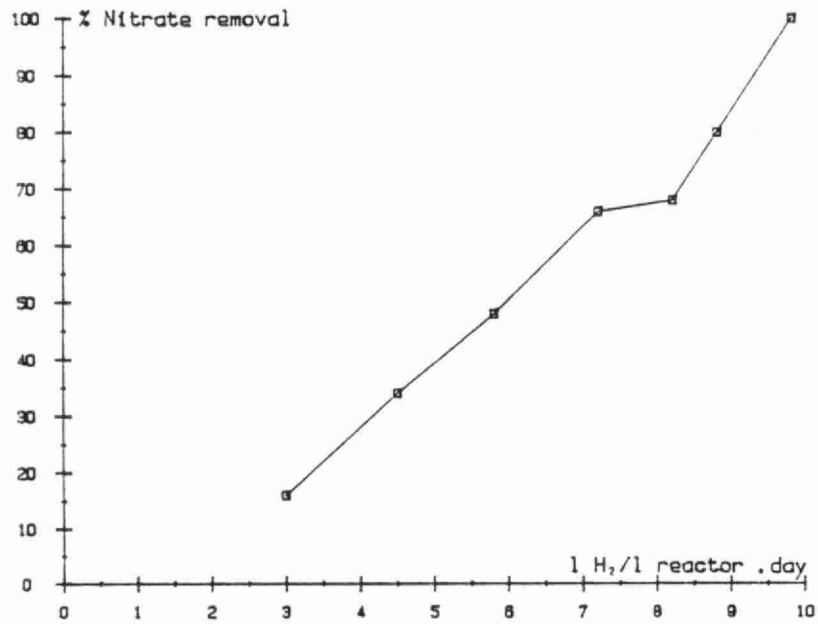

Fig. 2. Effect of the H_2 dosage on the efficiency of nitrate removal for water containing 50 mg NO_3^--N/l and at a volumetric loading rate of 0.5 g NO_3^--N/l r tot.d

TABLE 6 Operating Conditions for the Different Reactor Zones in Reactor System 1

	DN1	DNtot*	Total reactor**
Nitrate loading rate (g NO_3^--N/l reactor.d)	0.46	0.33	0.20
Hydraulic retention time (θH) (min)	154	218	353

* DNtot = DN1 + DN2
** Total reactor = DN1 + DN2 + Nitrification reactor

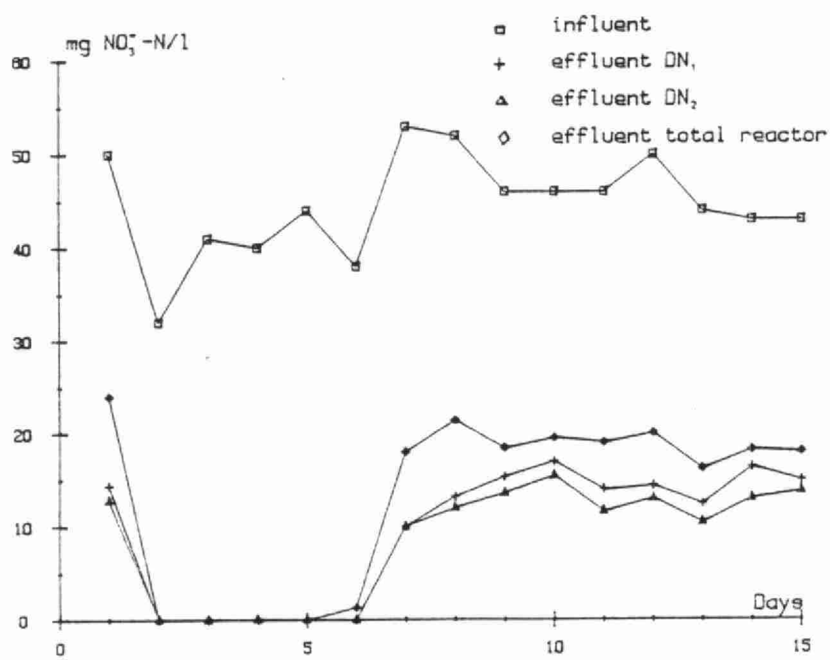

Fig. 3. Evolution of the NO_3^--N content for the different reactor zones in reactor system 1

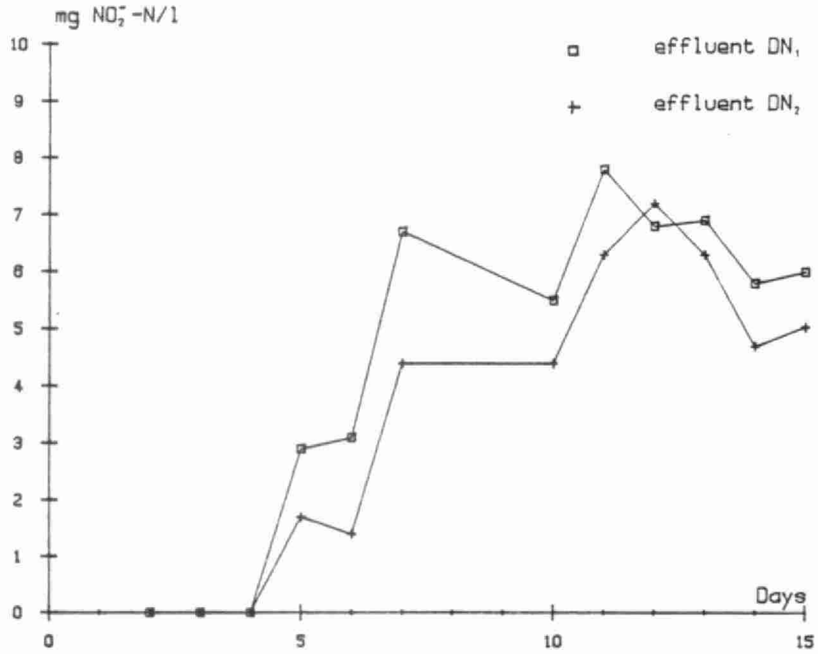

Fig. 4. Evolution of the NO_2^--N content for the DN1 and DN2 in the reactor system 1

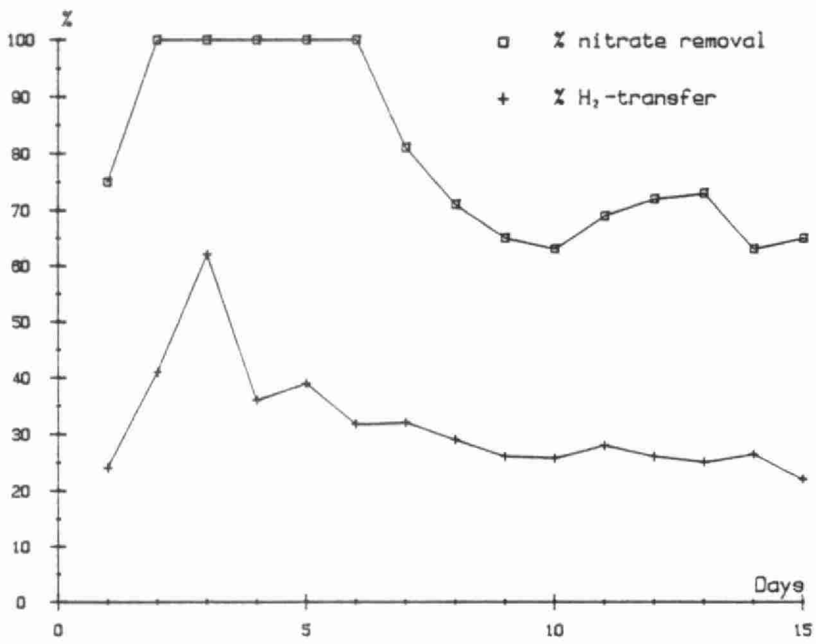

Fig. 5. Efficiency of nitrate removal and H_2 consumption for DN1 in reactor system 1

A biomass yield factor (Y = kg biomass (DW)/kg substrate removed (COD)), was calculated from the DW of the excess sludge weekly removed (= biomass growth per week) and the amount of H_2 used for denitrification in one week (expressed as COD). Thus, ca. 0.4 kg biomass DW was formed per kg COD removed. Due to this high cell yield several difficulties arose. The biomass accumulated very fast in and on the PU cubes. Hence, the diffusion of NO_3^--N and H_2 to the innerside of the cubes was hindered.

Another problem was the obstruction of the flow through of the water and the gas in the reactor. Due to the growth of the biofilm round the cubes, the initially separated cubes tended to "glue" together. This invoked the formation of preferential channels of the water and gas which strongly affected the overall nitrate removal capacity. Microscopical examination of the removed sludge revealed that the denitrifying biomass existed of rods and filamentous bacteria, also protozoa were present. The following bacteria were identified as true denitrifiers : Pseudomonas maltophilia and Pseudomonas putrefaciens. The removed sludge was white and good flocculating and had a SVI of 54 ml/g suspended solids.

Withholding the daily addition of 100 ml soil extract to the influent, led to a decrease of only 25 - 30 % nitrate removal. This indicated a mineral deficiency for the growth and maintenance of the denitrifying biomass when only nitrate enriched tap water was fed.

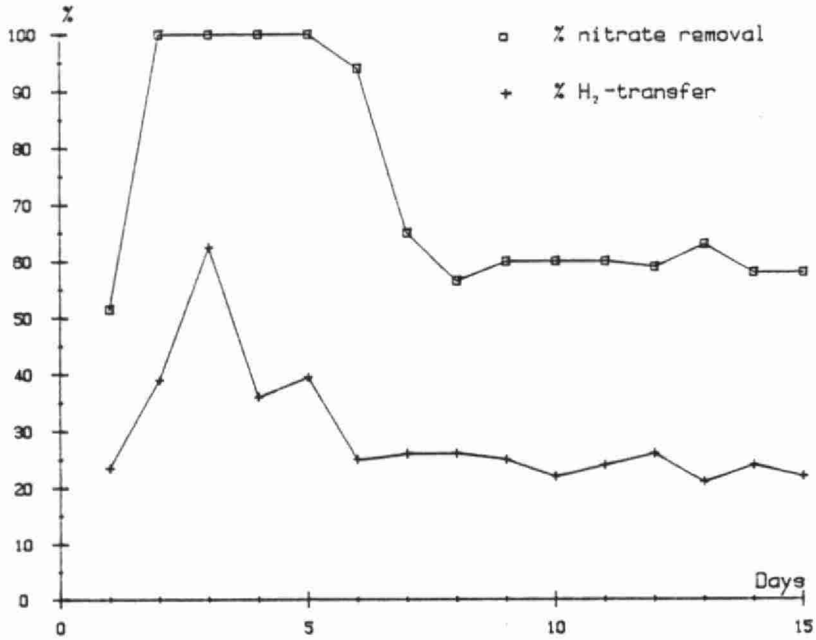

Fig. 6. Efficiency of nitrate removal and H_2 consumption for the total reactor in the reactor system 1

Process Performance of Reactor System 2

The operating conditions for the different reactor zones are described in Table 7 for a water containing 15 mg N/l. The liquid flow amounted to 72 l/d.

TABLE 7 Operating Conditions for the Different Reactor Zones in Reactor System 2

	DN1	DNtot*	Total reactor**
Nitrate loading rate ($g\ NO_3^-$-N/l reactor.d)	0.50	0.35	0.25
Hydraulic retention time (θH) (min)	43	61.5	85

* DNtot = DN1 + DN2
** Total reactor = DN1 + DN2 + Nitrification reactor

At the start, the total gasphase was flushed till 100 % H_2 was attained. Daily, about 11 l H_2 were supplied from the gasreservoir.

Hard water. The test was started with hard water with a NO_3^--N concentration of 15 mg/l (described in Table 3) as influent for the denitrification reactor. Due to the higher water flow compared to reactor system 1, the friction of the water on the biofilm was more intensive. Concomitantly, more biomass was washed out with the regular water flow. The excess biomass which had to be removed after scouring, amounted to 0.15 - 0.20 kg biomass DW/kg COD removed. Weekly sludge removal prevented clogging of the reactor. Nevertheless, after a few weeks, the test had to be stopped due to clogging of the DN1 by $CaCO_3$-precipitation on the PU carrier material. Denitrification did increase the pH of the effluent of the DN1 to 8.8 - 8.9. As a result, the saturation index rose to 1.6 - 1.8 as determined by the monogram of Hoover and the formula of Langlier (Van Haute, 1973). Hence, about 5 g $CaCO_3$ per day sedimented on the PU strips in the DN1.

Soft water. New PU strips were mounted to the DN1 and the test was repeated with soft water (see Table 4) as influent. During the first week, 100 ml of a culture of Alcaligenes eutrophus ATCC 17697 was daily added to the influent. After a growth period of 1.5 weeks, the efficiency of nitrate removal reached 100 % in the DN1 without nitrite accumulation. The % H_2 in the gasphase decreased in 5 days to 62 - 68 % and stabilized from then onwards. The efficiency of the H_2 consumption fluctuated around 40 - 45 %. A maximum nitrate loading rate of 1 g N/l reactor.d in the DN1 or 0.5 g N/lr tot.d was obtained. The liquid flow amounted to 142 l/d and the retention time was 22 min and 43 min in the DN1 and the total reactor resp. Daily, about 16 l H_2 were supplied from the gasreservoir. Under these conditions, the nitrate removal efficiency reached to 100 % in the DN1, without nitrite accumulation. The % H_2 in the gasphase dropped to 62 - 68 % within 2 days and stabilized. The efficiency of the H_2 consumption amounted to 50 - 55 %. The biomass yield factor amounted 0.1 - 0.15 kg DW/kg COD removed. The sludge removed had

a SVI of 47 ml/g suspended solids and the denitrifying biomass attained a concentration 12 g DW/1 reactor in the DN1. Bacteriological analyses on the effluent gave negative results with regard to total coli-bacteria, fecal coli-bacteria and fecal streptococci. The number of viable cells was 25.10^3/ml and the total amount of Pseudomonas spp. fluctuated around 10^3/ml.

DISCUSSION

Biokinetics of the H_2 Uptake

Solubility of H_2. Taking into account Henry's law :

$$c_s = \alpha \cdot p \qquad \text{(eq. 4)}$$

where c_s = saturation concentration of the gas in water (ml/l)
α = coefficient of absorption (ml/l) at 101.3 kPa
p = partial pressure of the gas in the gasphase (atm)

and the gas law :

$$\frac{p_o V_o}{T_o} = \frac{pV}{T} \qquad \text{(eq. 5)}$$

where V_o = 22.41 l (volume of 1 mole of gas at STP)
STP = Standard temperature and pressure
with T_o = 273°K
p_o = 101.3 kPa
V = volume of 1 mole of gas at T (K) and p (atm)

the solubility of H_2 in the DN1 is calculated. Table 8 gives the solubility of H_2 at the top of the DN1 in relation to its partial pressure and the temperature. The total pressure of the gasphase amounts to 101.3 kPa.

TABLE 8 Solubility of H_2 (mg/l) at the Top of the DN1 in Relation to its Partial Pressure and the Temperature

T (°C) \ pH_2 (kPa)	10.13	50.65	70.91	81.04	91.17	101.30
0	0.19	0.96	1.35	1.54	1.77	1.93
10	0.17	0.85	1.19	1.36	1.53	1.70
20	0.15	0.75	1.06	1.21	1.37	1.52
30	0.14	0.69	0.97	1.10	1.24	1.38

TABLE 9 Solubility of H_2 (mg/l) at the Bottom of the DN1 in Relation to its Partial Pressure and the Temperature

T (°C) \ pH_2 (kPa)	10.13	50.65	70.91	81.04	91.17	101.30
0	0.22	1.11	1.55	1.77	1.99	2.22
10	0.19	0.98	1.37	1.57	1.76	1.96
20	0.17	0.88	1.23	1.41	1.58	1.76
30	0.16	0.79	1.11	1.27	1.43	1.59

Diffusion of H_2 in water and in the biofilm. Williamson and McCarty (1976) developed a theoretical model of substrate utilization by bacterial biofilms. The model is based on two concepts : substrate diffusion from an aqueous phase into the biofilm and microbial transfer of the substrate in the biofilm. This biofilm model can be used only when a single species (either electron donor or electron acceptor) is both, flux and substrate limited across the entire biofilm. Williamson and McCarty (1976) presented two relationships for determining if single limitation occurs.

The electron acceptor is flux limiting if :

$$Soa < \frac{\nu a \cdot Dcd \cdot MWa}{\nu d \cdot Dca \cdot MWd} \cdot Sod \qquad \text{(eq. 6)}$$

The electron acceptor is substrate limiting if :

$$Sca < \frac{Ksa}{Ksd} \cdot Scd \qquad \text{(eq. 7)}$$

where
Soa, Sod = electron acceptor and -donor concentration in the bulk liquid (mg/l)
Sca, Scd = electron acceptor and -donor concentration at a specific depth in the biofilm (mg/l)
νa, νd = stoichiometric reaction coefficients for the electron acceptor and -donor
Ksa, Ksd = half-velocity coefficient for the electron acceptor and -donor (mg/l)
Dca, Dcd = diffusion coefficient within the biofilm for the electron acceptor and -donor (cm^2/d)
MWa, MWd = molecular weight of the electron acceptor and -donor

If it is assumed that lithotrophic denitrification, analogous to the heterotrophic denitrification (Klapwijk, 1978; Pitt and co-workers, 1981) obeys Monod kinetics, it can be determined whether H_2 is substrate and/or flux limiting. The diffusion coefficients of H_2 and $NaNO_3$ in water are 4.15 cm^2/d and 1.9 cm^2/d respectively (Perry and Chilton, 1974). The diffusion coefficients in the biofilm are approximately 0.9 times those in water (Williamson and McCarty, 1976).

For the lithotrophic denitrification :

νa = 2	νd = 5
MWa = 62	MWd = 2
Dca = 1.71	Dcd = 3.73
Ksa = 0.1 (Rittman and Dovantzisk, 1983)	Ksd = 0.0017 - 0.0054 (Conrad and Seiler, 1981)

With an influent concentration of 50 mg NO_3^--N/l or 221 mg NO_3^-/l and taking into account the solubility of H_2 (at partial pressure = 101.3 kPa and T = 20°C), the relationship (eq. 6) does not hold : 221 $\nless$ 41. So, H_2 will be flux limiting. From Soa >> Sod and Dca = 1/2 Dcd it can be expected that Sca >> Scd. So the relationship (eq. 7) does not hold either, despite the high affinity for H_2 (low Ksd value). Hence, H_2 will also be substrate limiting, even when its Ksd would be underestimated.
With an influent concentration of 15 mg NO_3^--N or 66 mg NO_3^-/l, the relationship (eq. 6) does not hold : 66 $\nless$ 41, so H_2 will still be flux limiting. Only, for the lower nitrate concentrations, eq. 7 may hold and consequently H_2 is not substrate limiting.

In general, it can be concluded that the electron donor is both flux and substrate limiting under the experimental conditions studied in reactor system 1. When the % H_2 in the gasphase dropped to 80 %, H_2 limited the denitrification of the high nitrate loaded water. However, the electron donor is not substrate limiting under the experimental conditions studied in reactor system 2. H_2 did not limit the denitrification of the low nitrate loaded water, even when the % H_2 in the gasphase decreased to 65 %.

Calculation of the % N_2 in the gasphase in relation to the amount of water denitrified per liter initial H_2.

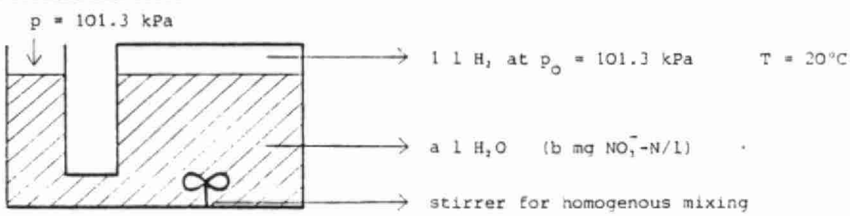

Fig. 7. Situation of the reactor at the start of the process

In principle, the reactor (Fig. 7) can be conceived as consisting out of two hydraulically communicating vessels. At the start, the gasphase above the waterlevel of the closed vessel is filled with H_2 gas. The overall denitrification reaction (eq. 3) shows that 1 l H_2 is sufficient for the reduction of 233 mg NO_3^--N to 0.199 l N_2, under the given experimental conditions of pressure (101.3 kPa) and temperature (20°C). At the start, part of the H_2 gas dissolves in function of its partial pressure (pH_2 = 101.3 kPa). This dissolved H_2 is totally consumed by the denitrifying microorganisms, and N_2 builds up. Consequently, the partial pressure of H_2 will decrease and the total gasvolume above the waterlevel will decrease:consumption of 5 moles H_2 creates only 1 mole N_2 and csN_2 (17.4 mg/l at 20°C) is greater than csH_2 (1.5 mg/l at 20°C). Less H_2 can dissolve in the new equilibrium, compared with the initial situation. The partial pressure of H_2 will systematically decrease till zero and the partial pressure of N_2 will increase. A mathematical model which takes account of these phenomena was developed as follows :

$$piH_2 \cdot csH_2 \cdot a = ri \qquad \text{(eq. 8)}$$

At the onset, the mass balance for H_2 between the gas- and waterphase is brought in equilibrium due to partially dissolving of the H_2 (ri = ml H_2 dissolved)

$$\frac{ri}{5} = si \qquad \text{(eq. 9)}$$

All the dissolved H_2 is consumed for denitrification what creates the build up of N_2 gas (si = ml N_2 built up)

Before the new equilibrium :

$$V_o - \sum_{x=1}^{i} r_x + \sum_{x=1}^{i} s_x = V_i' \qquad \text{(eq. 10)}$$

Due to denitrification the initial gasvolume V_o has changed. V_o is corrected for the total amount of H_2 gas consumed and N_2 gas built up (Vi' = ml gas before the new equilibrium)

$$p_i' tot = \frac{V_i''}{V_o} \cdot p_o tot$$ (eq. 11) Due to the decrease of the gasvolume V_o to V_i'', the total gaspressure is decreased (p_i' tot = total gaspressure (kPa))

$$p_i' N_2 = \frac{\sum_{x=1}^{i} s_x}{V_i''} \cdot p_i' tot$$ (eq. 12) The build up of N_2 gas creates a partial pressure in the gasphase of N_2 ($p_i' N_2$ = partial pressure of N_2 (kPa))

$$\sum_{x=1}^{i} s_x - c_s N_2 \cdot p_i' N_2 \cdot a = t_i$$ (eq. 13) The partial pressure of N_2, calculated in eq. 12 brings in equilibrium the mass balance for N_2 between the gas- and waterphase (t_i = ml N_2 in the gasphase)

After the new equilibrium has been reached :

$$V_i' - \sum_{x=1}^{i} s_x + t_i = V_i$$ (eq. 14) The gasvolume V_i'' , calculated before the equilibrium is corrected for the amount of N_2 in the gasphase after the equilibrium (V_i = ml gas after the new equilibrium)

$$p_i tot = \frac{V_i}{V_i''} \cdot p_i' tot$$ (eq. 15) Due to the decrease of the gasvolume V_i' to V_1, the total gaspressure is decreased (p_1 tot = total gaspressure (kPa))

$$p_i N_2 = \frac{t_i}{V_i} \cdot p_i tot$$ (eq. 16) The partial pressure of N_2 ($p_i' N_2$), calculated before the new equilibrium, is corrected for the amount of N_2 present in the gasphase after the equilibrium ($p_i N_2$ = partial pressure of N_2 (kPa))

$$\frac{t_i}{V_i} \cdot 100 = Y_i$$ (eq. 17) Taking into account the total gasvolume and the amount of N_2 in the gasphase after equilibration, the % N_2 in the gasphase is calculated (Y_i = % N_2 in the gasphase)

$$\frac{\sum_{x=1}^{i} r_i \cdot u}{1000 \cdot b} = X_i$$ (eq. 18) Taking into account the total amount of H_2 dissolved (= consumed) in the water (l) and the concentration of NO_3^--N in the water (b) (mg/l), the amount of water denitrified is calculated (X_i = l H_2O denitrified)

$$p_i tot - p_i N_2 = p_{(i+1)} H_2$$ (eq. 19) Due to the build up of a partial pressure of N_2 in the gasphase (eq. 16), and the decrease of the total gaspressure (eq. 15), the partial pressure of H_2 in the gasphase is decreased ($p_{(i+1)} H_2$ = partial pressure of H_2 after the new equilibrium (kPa))

For i = 1 till i where $p_{(i+1)} H_2 > 0$

Where $c_s H_2$ = 18.2 ml/l (solubility of H_2 at pH_2 = 101.3 kPa and T = 20°C)
$p_1 H_2 = p_o$ = 101.3 kPa
V_o = 1000 ml
$c_s N_2$ = 15.5 ml/l (solubility of N_2 at pN_2 = 101.3 kPa and T = 20°C)
u = 233 mg NO_3^--N/l initial H_2

The model is conceived for denitrification at 20°C. The resulting X_i and Y_i data are plotted in Fig. 8 for different a - b values. For each nitrate concentration tested, the experimental gas stabilization zone is marked on Fig. 8.

For high nitrate loaded water (50 mg N/l) the experimental gas stabilization zone was found around 20 - 25 % N_2 in the gasphase. Curve 1 (Fig. 8) indicates that above 25 % N_2 in the gasphase, the further enrichment of the gasphase on N_2 proceeds increasingly faster per liter of denitrified water. When the % H_2 in the gasphase was 80 %, there was still a nitrate removal of 60 % in the total reactor. Despite this continuous creation of N_2 gas, the % N_2 in the gasphase stabilized at about 20 - 25 %. Indeed, at that stage an equilibrium will be reached where the amount of N_2 formed by denitrification will be about equal to the amount of N_2 dissolvable in the influent at the actual partial pressure of N_2.
The partial pressure of H_2 will decrease rapidly and with this the solubility of the electron donor once the % N_2 in the gasphase has reached 20 - 25 %. The test results of reactor system 1 indeed confirm that H_2 limits the denitrification of high nitrate loaded water when its percentage in the gasphase has decreased to 80 % or less.
For low nitrate loaded water (15 mg N/l) the experimental gas stabilization zone was found around 32 - 38 % N_2 in the gasphase (test results of reactor system 2). Curve 3 (Fig. 8) indicates that above 38 % N_2 in

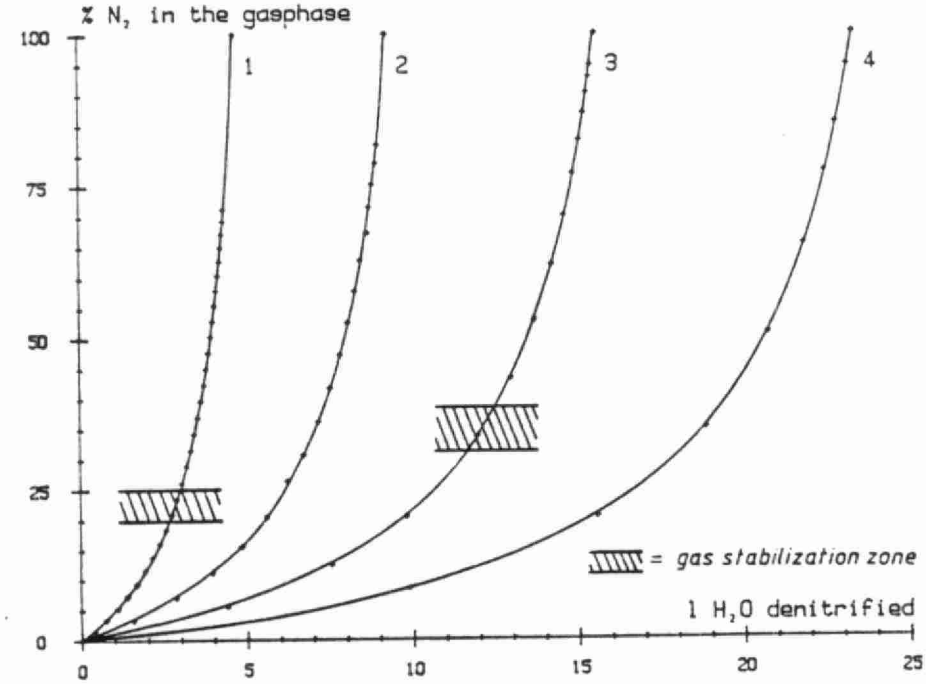

Fig. 8. Relation between the amount of water denitrified and the percentage N_2 in the gasphase for different nitrate concentrations (b) and different l H_2O to denitrify (a) at 1 l H_2 initially in the gasphase

Curve 1 : a = 4.66 l b = 50 mg NO_3^--N/l
Curve 2 : a = 9.23 l b = 25 mg NO_3^--N/l
Curve 3 : a = 15.23 l b = 15 mg NO_3^--N/l
Curve 4 : a = 23.30 l b = 10 mg NO_3^--N/l

in the gasphase, the further enrichment of the gasphase on N_2 proceeds faster per liter denitrified water. When the % H_2 in the gasphase was 32 - 38 %, there was still a nitrate removal of 100 % in the total reactor, but no further increase of the % N_2 in the gasphase was observed despite the continuous creation of N_2. So, at that stage the equilibrium was reached for the low nitrate loaded water. As confirmed by the test results of reactor system 2, H_2 did not limit the denitrification reaction at the equilibrium.

General Applicability

The present reactor configuration was developed to provide a technology to denitrify ground and surface water to produce drinking water. The described process is not directly advisable for denitrification of high nitrate loaded waters (> 50 mg N/l). The maximum denitrification rate amounts only to 0.2 g N/lr tot. d under optimal conditions (i.e. 80 % H_2 or more in the gasphase). In that case, the efficiency of nitrate removal amounts to 80 - 100 % and the efficiency of the H_2 consumption reaches 30 - 40 %. The volumetric loading rate thus obtained is too low compared to the rates obtained by other denitrification systems, especially heterotrophic denitrification systems. For instance, Timmermans (1983) tested a fluidized bed reactor for heterotrophic denitrification of drinking water. In a first test, methanol was added as C-source, in a second test, ethanol was used as C-source. The denitrification rate at 20°C reached to 21 g N/l reactor.d and 10 g N/l reactor.d respectively. Heterotrophic denitrification in a suspended bed reactor with methanol as C-source attained a denitrification rate of 3 g N/l reactor.d at 20°C (Gauntlett, 1981).
Kurt and co-workers (in press) studied a fluidized bed reactor with H_2 as a reductant. The denitrification rate amounted to 0.13 g N/l reactor.d for water containing 50 mg N/l and for a residence time of 10.3 hours. Remarkable was the high nitrite accumulation of 47 mg NO_2^--N/l in the effluent. Gros and co-workers (1982) tested a fixed bed reactor sparged with H_2 gas and with a strip system as carrier for the microbial biomass. The residence time in the reactor amounted at least 2 hours to reduce the nitrate content of the influent from 11.3 mg N/l to 5 mg N/l without nitrite accumulation, at a volumetric loading rate of only 0.12 g N/lr tot.d. A reactor system with indirect H_2 input and recirculation of the water was studied by Ginocchio (1980). With an influent concentration of 16 mg N/l and a residence time of 20 minutes, a denitrification rate of 0.8 g N/l reactor.d was reached. No specifications of the H_2-dosage and the efficiency of the H_2 gift are available. All of these lithotrophic denitrification systems described, do not contain a build-in post-denitrification and reaeration phase. They still need an aeration step during the post-treatment of the effluent. The present configuration is such that the finally produced water is reaerated and free of reduced metabolites.

The cubic PU sponges, as used in reactor system 1, are not advisable as carrier material for the denitrifying biomass. The separated cubes tend to grow into one piece and this gives diffusion and flow through problems. These problems can be avoided by the use of strips of PU sponges as carrier material, as was the case for reactor system 2.
Preferably, the nitrate loaded water contains little or no suspended solids. It can, but does not have to contain biodegradable organics. Denitrification of hard water gives rise to clogging of the DN1 by $CaCO_3$ sedimentation. In order to prolong the life-time of the reactor, the pH of the incoming water should be adjusted so that the saturation index in the DN1 remains below 1.

The reactor system 2 operated with soft and low nitrate loaded water (≤ 15 mg N/l) yielded satisfactory results. For a volumetric loading rate of 0.5 g N/lr tot.d, the nitrate removed amounted to 100 % and no nitrite accumulation was observed. The efficiency of the H_2 consumption reached 50 - 55 %. A stabilization in the gascontent was reached when the % N_2 in the gasphase amounted 32 - 38 %. This had no negative effect on the efficiency of nitrate removal and H_2 consumption. Due to the nitrification zone in the last part of the reactor, the final effluent was oxygen-rich. This effluent also satisfied the bacteriological requirements for drinking water. Weekly sludge removal avoided all problems of clogging of the reactor due to biomass accumulation.

A major advantage of the present method is that the reductant H_2, added to the water, is non-toxic and due to its low solubility can not be overdosed. In heterotrophic denitrification reactors, an organic C-source is added to the incoming water. These reductants dissolve in the water and thus have to be completely removed by the denitrification process. Otherwise, they reduce the quality of the drinking water produced. Restconcentrations of these organic C-sources can cause bacterial aftergrowth in the water supply system. Especially when methanol is used as C-source, there is the possible toxicity of residual levels of methanol in the drinking water. To prevent residual levels of added C-source, the effluents of the heterotrophic denitrification systems require extensive post-treatment such as aeration to increase the DO level, biofiltration to oxidize residual levels of the C-source and desinfection to eliminate microorganisms (Klapwijk and Van Der Hoek, 1985). The denitrified oxygen-rich effluent of the reactor system 2 only requires a desinfection step.

The system presented for denitrification of low nitrate loaded water can be seen as an extensive and safe method for small and medium size treatment plants. For high nitrate concentrations, a two-phase denitrification system may be advisable consisting of a heterotrophic denitrification unit working under C-limitation and removing the main part of the nitrate. A lithotrophic reactor with H_2 gas can then be implemented to remove the rest concentrations and also to provide an extra safety in case the organic reductant dissolved is not completely converted.

ACKNOWLEDGEMENTS

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Project Title:

FEASABILITY OF THE REMOVAL OF CHLORITE ION
WITH ACTIVATED CARBON

Contact (name of person, organization, address, telephone):

Dr. W.J. MASSCHELEIN
Director of the Laboratories
Brussels Intercommunal Waterboard
Chaussée de Waterloo 764
B - 1180 BRUSSELS
(BELGIUM)

Project Description (Please attach a schematic diagram if appropriate):

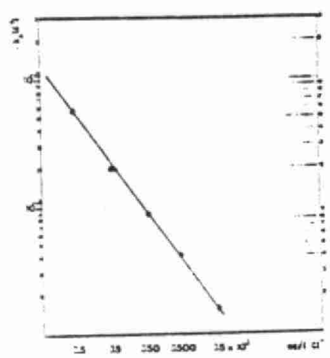
The kinetics of the removal of ClO2- by reaction with activated carbon is of second order

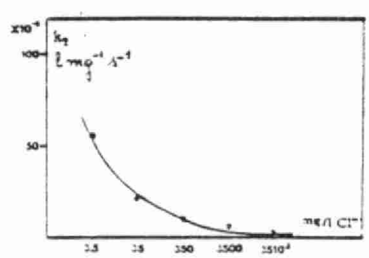
$$ClO_2^- + C^* \rightarrow \text{products}$$

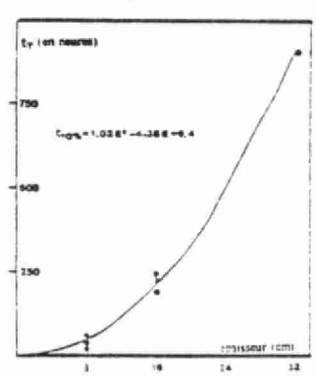
$$-\frac{d\,|ClO_2^-|}{dt} = k_2\,|ClO_2^-|\,|C^*|$$

$$\log \frac{|C^*|_t}{|ClO_2^-|_t} = \log \frac{|C^*|_0}{|ClO_2^-|_0} + \frac{1}{2.3}\left(|C^*|_0 - |ClO_2^-|_0\right)k_2 t$$

The reaction can be of apparent first order if a large excess of carbon remains present. Chloride ion promotes competitive inhibition in both processes (figures given). The operational autonomy ranges at least one year per meter GAC at an inlet concentration of 1 mg/l ClO2- (fig). Different carbons show differences in reactivity.







Operating and cost data (including data on efficiency, results, etc.):

No extra cost compared to the adsorption process has been established yet.

Place(s) of installation/application (including dates):

Use of the powdered carbon process at the TAILFER plant of the BRUSSELS' INTERCOMMUNAL WATERBOARD

Patent status, if applicable:

open

Other information (e.g., funding source, cooperating agencies, etc.):

paper attached (in French)

If available attach descriptive publications, technical literature, manufacturers' specification, patent descriptions, etc.

SUR L'ÉLIMINATION DE L'ION CHLORITE AU MOYEN DE CHARBON ACTIF

THE REMOVAL OF CHLORITE BY ACTIVATED CARBON

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RÉSUMÉ

La présente contribution traite des conditions et des possibilités d'élimination de l'ion chlorite de l'eau au moyen de charbon actif.

Pour le charbon actif en poudre utilisé à des concentrations recontrées dans un décanteur à lit de boue, la cinétique de réaction est du premier ordre apparent et les constantes de l'ordre de 10^{-3} s^{-1}. Cependant la réaction est en fait d'ordre deux et le charbon, ou du moins certains de ses sites actifs, constitue un partenaire réactionnel. L'ion chlorure constitue un inhibiteur compétitif pour les sites actifs dont l'action se développe d'une manière analogue aux inhibitions compétitives de réactions enzymatiques.

En pratique, une élimination de l'ordre de 25 à 30 % est obtenue dans un décanteur à lit de boue.

L'élimination de l'ion chlorite sur des filtres à charbon actif granulé se fait à la vitesse habituelle d'une filtration sur des filtres à adsorption, jusqu'à plus de 4 ans pour 2 m de couche filtrante. Cette méthode s'avère donc efficace. De plus, l'épuisement des filtres est davantage le résultat de phénomènes d'adsorption que de la réaction avec l'ion chlorite.

SUMMARY

This contribution concerns the conditions underlying the possible removal by activated carbon of chlorite from water.

The reaction kinetics, when using powdered activated carbon in the concentration range as exists in a settling tank with a sludge blanket, is of first order with a constant in the range of 10^{-3} s^{-1}. However, it is demonstrated that the reaction is in fact of second order and therefore the carbon, or at least certain of its active sites, forms a reactionnal partner. Chlorite inhibits the reaction by competition for active sites, and this can be described by the formula which is applied

to enzymatic reactions.

In the practical operation of a sludge contact clarifier, the removal rate of chlorite ranges between 25 and 30 %.

When the removal of the chlorite ion is carried out on granular activated carbon filters and operated at a filtration velocity suited to adsorption, autonomy of operation may attain 4 years for a 2 m filtration layer. The method appears to perform very well. Moreover, the exhausting of the filters is more the result of adsorption than of chlorite ion reactions.

INTRODUCTION.

La question envisagée dans cette contribution concerne principalement les modalités de l'utilisation du dioxyde de chlore dans le traitement des eaux de surface. Dans ce dernier, l'emploi du dioxyde de chlore en prétraitement au lieu de celui du chlore évite ou limite la formation de dérivés organohalogénés, tout en réalisant une oxydation-désinfection adéquate conjointement à un traitement physico-chimique par coagulation-floculation. En pratique, les dosages de ClO_2 fluctuent entre 1 à 2 mg/l et peuvent très exceptionnellement atteindre 3 à 5 mg/l. Cette application se distingue donc fondamentalement de l'utilisation du dioxyde de chlore en désinfection finale pour la potabilisation qui engage des concentrations généralement inférieures à 0,25 mg/l.

Le dioxyde de chlore conduit à l'ion chlorite par réduction partielle. La dismutation alcaline en chlorite et chlorate peut intervenir éventuellement de manière secondaire. Parallèlement, la dismutation neutre ou acide du dioxyde de chlore peut engendrer la formation de chlorates et de chlorures (1, 2). Antérieurement, nous avons formulé une règle pratique d'ajustement de la dose de traitement (2, 3) selon laquelle le rapport en poids des ions ClO_2^-/ClO_3^- contenus dans l'eau traitée doit rester supérieur à 1. Dans ce cas, la concentration en ion chlorite issu des réactions peut atteindre 0,5 à 1 mg/l.

Le chlorite résiduel peut être toxique par la formation de méthémoglobine. Toutefois, la dose létale pour le rat est de LD 50 = 140 mg/kg (exprimée en chlorite de sodium) (1). Il semble donc que le risque de toxicité aiguë due au chlorite issu du dioxyde de chlore est pratiquement négligeable. En milieu clinique, des investigations récentes sur des sujets humains n'ont pas montré d'effets métaboliques ou sanguin nuisibles après une durée de l'ordre d'un mois et une ingestion chronique de 5 mg/l de l'ensemble des composés oxychlorés concernés (ClO_2, ClO_2^-, ClO_3^-) (27). Cependant, il reste indiqué que la concentration résiduelle de l'ion chlrotie n'excède pas 0,5 mg/l comme limite de sauvegarde contre des goûts astringents dans l'eau. De plus, aux U.S.A., l'agence fédérale EPA a recommandé de limiter l'ensemble des dérivés oxychlorés inorganiques de l'eau potable à moins de 0,5 mg/l (4).

Dans certains cas concrets, comme celui du traitement d'eau de Meuse à l'usine de Tailfer qui alimente en partie l'agglomération bruxelloise, le chlorite résiduel du prétraitement au bioxyde de chlore est oxydé en chlorate lors de l'ozo-

nation finale. Le processus opère en deux phases (2) et comprend la formation intermédiaire de bioxyde de chlore.

* L'élimination de l'ion chlorite par le charbon actif constitue une voie alternative peu connue, dont la faisabilité est l'objet de la présente étude.

I - DONNÉES ANTÉRIEURES

* Une seule étude rapporte la décomposition de l'ion chlorite sur le système réactionnel ternaire composé de chlorite/charbon actif/produits organiques adsorbés (4). Pour ces derniers, l'acide vanillique et l'indane ont été retenus comme substances modèles. A noter que les conditions expérimentales de cette investigation engagent des concentrations de chlorite de 10 à 500 mg/l. Dans ces conditions, le taux de chargement maximal du charbon (Calgon ou Chemviron 400) en chlorite atteint 80 à 90 mg/g. Cette étude envisage la réduction du chlorite en chlorure avec, conjointement à une modification de la surface du charbon. Celui-ci deviendrait ainsi capable d'induire des réactions d'hydroxylation et de décarboxylation des substances organiques avec une ouverture secondaire de cycles aromatiques.

* Une recherche de 1965 (5) mentionne la stabilité apparente du chlorite et du dioxyde de chlore lors de la filtration sur charbon actif en grains. Elle décrit une méthode de préparation de dioxyde de chlore pur par mélange de chlorite de sodium et de charbon actif en poudre mais l'auteur assiste le processus par une acidification complémentaire.

* Dans une investigation précédente (6), nous avons établi que cette réaction reste peu importante dans la pratique du traitement d'eau. Il est à signaler cependant que les anhydrides organiques réagissent avec le chlorite en solution pour former le dioxyde de chlore (7, 8) selon la réaction :

$$4\ NaClO_2 + 2\ (R\ CO)_2O + H_2O = NaClO_3 + NaCl + 2\ R\ COOH + 2\ R\ COONa$$
$$+ 2\ ClO_2$$

Certains charbons, susceptibles d'être porteurs de groupements anhydrides ou similaires comme les lactones, seraient-ils capables de conduire à la formation de dioxyde de chlore ?

* La décomposition du dioxyde de chlore sur charbon actif, soumise à l'investigation au départ de solutions contenant 30 à 35 mg/l en présence de 20 à 100 mg/l de charbon actif, correspond à un processus comportant au moins deux phases consécutives d'une durée de demi-vie respective de l'ordre de 20 min. et de 3 h. Chacune des deux phases peut être décrite empiriquement par des équations cinétiques correspondant à des processus élémentaires du premier ordre mais se combinant en un ensemble évoluant selon une équation de puissance ($C/C0 = b\ c^{at}$) (6).

Le système (ClO_2 - charbon - composé organique adsorbé) constitue un système réactif ternaire ; notamment en présence d'hydrocarbures adsorbés sur le charbon, des dérivés organo-halogénés peuvent être produits qui ne se seraient pas formés en absence de charbon actif (9).

* Les recherches résumées ci-dessus constituent l'essentiel des connaissances sur la réaction du chlorite et du dioxyde de chlore sur charbon actif. Il reste à mentionner que des observations en usine de filtration sur charbon actif en grains ont permis de constater quelquefois l'élimination de l'ion chlorite par ce processus (10).

* On pourra, en outre, tirer profit des recherches plus nombreuses sur l'élimination du chlore et des chloramines par le charbon actif dans l'interprétation des résultats (11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22). A noter toutefois que la plupart de ces investigations se rapportent à la décomposition du chlore actif présent à des concentrations de plusieurs dizaines de mg par litre (11).

II - MATÉRIEL ET MÉTHODES

1 . Des suspensions de charbon actif en poudre représentatives des variantes habituellement approvisionnées pour le traitement des eaux de surface sont agitées avec une solution de chlorite. Cette dernière est obtenue par dissolution de chlorite commercial d'une teneur de 300 g/l en chlorite de sodium (env. 25 % en poids), dans une eau de référence (a). La diminution de la concentration en chlorite en fonction du temps de contact est mesurée par détermination polarographique sur une aliquote filtrée (23). Le charbon testé est principalement le produit NORIT W. 20 (b), mis en œuvre pour le traitement de l'eau de Meuse à l'usine de Tailfer. A titre indicatif, des données sont fournies pour les produits concurrentiels, CECA Acticarbone TK (c), Anthrosorb CC 100 (d) et un charbon pour usage en laboratoire, Baker A 498 Q (e). La gamme des concentrations prospectées correspond à celle existante dans un décanteur à lit de boue du type pulsator. Dans celui-ci, le facteur de concentration du charbon injecté atteint la valeur de 50 à 100 fois.

2. La stoechiométrie de la réaction du chlorite avec le charbon est déterminée par réaction du charbon NORIT W 20, introduit dans un litre d'eau de référence contenant de 5 à 50 mg/l de l'ion chlorite, ainsi que par des essais à concentration croissante en chlorite traité par une suspension à 300 mg/l de charbon.

3. L'effet de sel commun, le chlorure, est testé par la méthode des ajouts de NaCl à l'eau distillée et par un traitement de 1 mg/l de ClO_2^- par 200 mg/l de

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(a) Eau du puits de Waterloo de la CIBE, OMS : GEMS/WATER OPERATIONAL GUIDE, Geneva 1978 (Station number 051-006).

(b) NORIT, Nijverheidsweg Noord 72, NL - 3812 - PW AMERSFOORT.

(c) CECA, avenue Morane-Saulnier 11, F-78140 VELIZY-VILLACOUBLAY.

(d) Thomas NESS, Nantgarw, CARDIFF CW, 474 H.

(e) BAKER, 222 Red School Lane, Phillipsburg, NJ-08865.

charbon actif du type NORTI W 20.

4. Un test d'orientation se rapporte à la faisabilité de l'élimination de l'ion chlorite par filtration sur charbon actif granulé NORIT ROW o.8 SUPRA engagé dans une colonne expérimentale (Figure I). La vitesse de percolation pratiquée est celle de la filtration rapide. Au cours des différents essais, elle fut toujours comprise entre 1,25 et 1,35 mm/s.

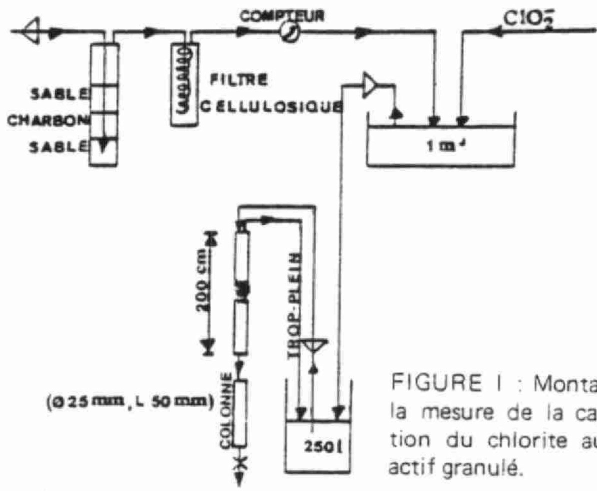

FIGURE I : Montage expérimental pour la mesure de la capacité de transformation du chlorite au moyen de charbon actif granulé.

III - RÉSULTATS EXPÉRIMENTAUX

L'ensemble des tableaux I, II, III, IV et V comprend les données expérimentales les plus importantes. Les données complémentaires sont reprises dans les graphiques d'interprétation, à titre indicatif seulement.

t(s)	$\left.\lvert C \right\rvert_o$: concentration en charbon (mg/l)				
	100	200	300	400	500
0	1	1	1	1	1
60					0.48
150				0.54	0.18
300	0.76	0.58	0.33	0.30	0.04
450				0.16	-
600	0.65	0.41	0.19	0.08	
750				0.05	
900	0.55	0.26	0.08	0.03	
1200	0.48	0.18	0.05	-	
1500	0.42	0.13	0.02	-	
1800	0.37	0.09	-	-	

TABLEAU I : Cinétique de la diminution de la concentration en chlorite en présence de charbon NORIT W 20. (Concentration initiale ClO_2^- 1 mg/l).

TABLEAU IV : Stoechiométrie de la réduction du chlorite sur charbon actif.

$\lvert C^* \rvert_o$ mg/l	$\lvert ClO_2^- \rvert_o$ mg/l	t(s)	$\lvert ClO_2^- \rvert_t$ mg/l	ΔCl^- mesurée mg/l
300	5	7200	0.23	2.4
300	10	10800	0.84	4.2
300	20	18300	3.32	9.2
300	30	25200	5.7	13.1
1000	50	2400	4.5	22.8

TABLEAU V : Effet de concentration ajoutée en ion chlorure dans de l'eau distillée sur la réduction de l'ion chlorite.

$\lvert Cl^- \rvert$ mol/l / t(s)	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}
0	1	1	1	1	1
300	0.91	0.72	0.46	0.42	0.35
600	0.79	0.56	0.32	0.22	0.20
900	0.73	0.44	0.16	0.13	0.08
1200	0.63	0.33	0.11	0.09	0.06
1500	0.58	0.23	0.07	0.04	0.04
1800	0.51	0.18	-	-	-

TABLEAU II : Cinétique de diminution de la concentration en ion chlorite, en proportion variable par rapport au charbon (Concentrations en mg/l).

$\frac{\lvert ClO_2^- \rvert_o}{\lvert C^* \rvert_o}$ / t(s)	$\frac{0.5}{100}$	$\frac{0.5}{200}$	$\frac{0.5}{500}$	$\frac{0.2}{100}$
150	-	-	0.16	-
300	0.4	0.25	0.11	0.13
450	-	-	0.05	-
600	0.33	0.07	-	0.10
900	0.28	0.06	-	0.08
1200	0.23	0.04	-	0.05
1500	0.19	-	-	0.04
1800	0.17	-	-	-

TABLEAU III : Détermination du taux de chargement maximal du charbon en chlorite (NORIT W 20, 300 mg/l, temps de contact : 48 h).

$\lvert ClO_2^- \rvert_o$ mg/l	$\lvert ClO_2^- \rvert_{48\,h}$	$\frac{\lvert ClO_2^- \rvert}{m}$
50	12	0.127
100	42	0.193
200	118	0.27
300	203	0.32
500	370	0.43
	limite	0.45
$\log \frac{\lvert ClO_2^- \rvert}{m} = 0.28 + 0.34 \log \lvert ClO_2^- \rvert_{48}$		

Les résultats mesurés sur les effluents de la colonne garnie de charbon en grains sont indiqués dans la Figure II. Ils concernent, sauf indication contraire, le charbon NORIT ROW 0.8 supra. La préfiltration sur colonne de sable, garantissant une bonne répartition hydraulique sur la colonne de charbon, reste facultative et sans effet sur les courbes de percement. Toutes les vitesses de percolation étaient comprises dans les limites de 1.3 ± 0.05 mm/s.

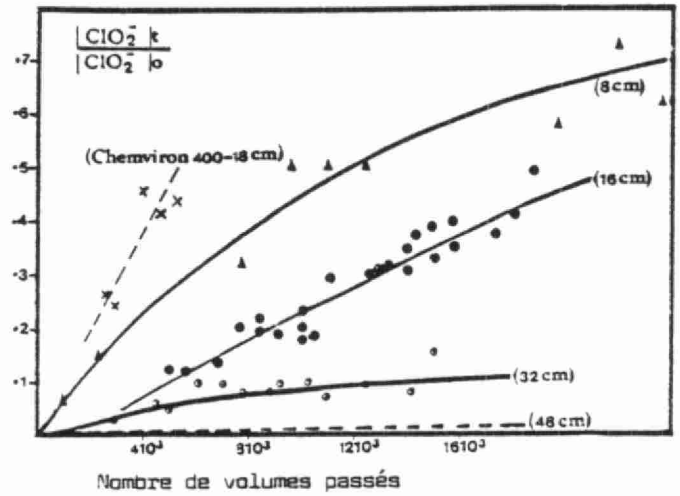

FIGURE II : Courbes de percement de l'ion chlorite d'une colonne garnie de charbon ROW 0.8 supra (NORIT) par rapport au volume de la colonne vide ; concentration initiale : 1 mg/l en ClO_2^-).

Les données de la Figure II concernent des expériences effectuées consécutivement en remplissant en partie la colonne d'adsorption à concurrence de l'épaisseur de couche indiquée.

IV - DISCUSSION

Dans la plupart des études décrites dans la littérature, la décomposition du chlore actif libre (14, 16) ou des chloramines (17, 19, 20) est rapportée comme un processus du premier ordre par rapport au chlore dissous. La première hypothèse consiste donc à appliquer le formalisme d'une cinétique du premier ordre à l'élimination du chlorite :

$$-\frac{d\,[ClO_2^-]}{dt} = -k'_a\,[ClO_2^-]$$

$$\text{et } \log\frac{[ClO_2^-]}{[ClO_2^-]_o} = -\frac{k'_a}{2.3}\,t = -k_a t$$

Cette hypothèse, appliquée aux données du Tableau I, fournit l'interprétation illustrée dans la Figure III.

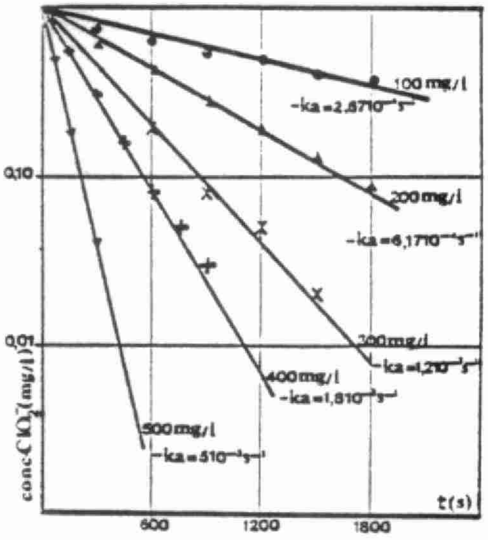

FIGURE III : Réduction selon un processus apparent du premier ordre de l'ion chlorite sur charbon actif en poudre.

On y relève l'absence d'une phase initiale rapide décrite pour le chlore (6, 14, 15, 16), le bioxyde de chlore (6) et les chloramines (21). Nous observons cependant une nette relation entre la constante cinétique du premier ordre et la concentration en charbon actif dans le milieu réactionnel. Cette relation s'exprime par les graphiques repris dans la Figure IV.

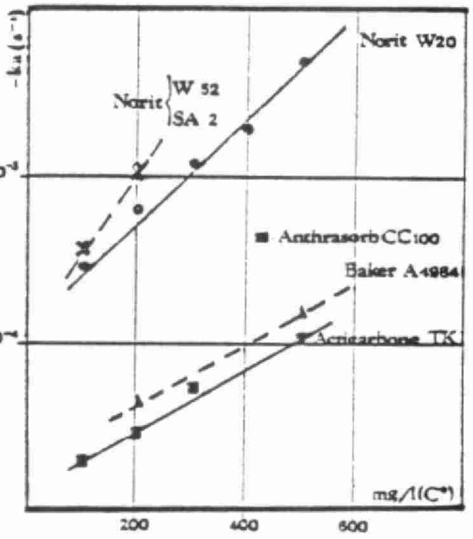

FIGURE IV : Dépendance de la constante cinétique apparente du premier ordre de la réduction de l'ion chlorite, de la concentration en charbon actif.

Bien que la réduction du chlore et des chloramines au moyen de charbon actif soit généralement considérée comme un processus du premier ordre, l'intervention du charbon comme partenaire réactionnel est manifeste. De plus, la constante cinétique du premier ordre de décomposition du chlore est inversement proportionnelle à la taille des grains (14). Lors de la réduction du chlore, la surface microporeuse (BET) diminue jusqu'à 50 % de la valeur initiale. L'hypothèse retenue pour expliquer ce phénomène est un élargissement des pores via cette réaction et, secondairement, un blocage par formation d'oxydes à l'entrée de ceux-ci (15). Aussi fut-il observé que l'efficacité d'élimination des chloramines contenues dans une eau percolée sur ce support augmente quand les dimensions des particules de charbon diminuent (19). Ce phénomène peut être interprété par la facilité d'accès aux pores, dont la longueur moyenne est plus petite pour les petits grains (21). On estime en effet que la demi-longueur des pores est de l'ordre du sixième de la moyenne géométrique des diamètres des grains (19). Dans ce même contexte, l'énergie d'activation de la réaction globale dichloramine-charbon est de l'ordre de 35 kJ/mole (19), tandis que pour le chlore libre, les mesures expérimentales se situent entre 39 et 51 kJ/mole. Ces valeurs correspondent à celles généralement attendues pour les réactions contrôlées par des phénomènes de diffusion.

Si les données reprises dans la Figure IV permettent une évaluation de l'effet de différents charbons en poudre en fonction de la concentration mise en œuvre, une interprétation en reste nécessaire.

Dans le cas de solutions relativement concentrées de chlore libre, la constante cinétique de décroissance du premier ordre a été mise en corrélation linéaire avec le taux de chargement du charbon en équilibre avec la solution, c'est-à-dire la valeur de $\frac{x}{m}$ en g/g (15).

Nous ne retrouvons pas la même corrélation dans le cas du chlorite. Il faut observer que nous travaillons dans des conditions beaucoup plus proches de celles de la pratique, soit un large excès de charbon par rapport à l'oxydant. Dans ces conditions, nous observons une corrélation logarithmique entre la constante cinétique apparente du premier ordre et la concentration de charbon mis en œuvre. La réaction semble donc de pseudo-premier ordre.

Pour compléter l'interprétation des données de manière plus fondamentale, nous envisageons aussi l'hypothèse d'une réaction bimoléculaire dans laquelle le charbon actif intervient comme partenaire réactionnel à part entière dans la cinétique d'élimination du chlorite.

Le processus du deuxième ordre est décrit par :

$$ClO_2^- + C^* \rightleftharpoons \text{produits}$$

$$-\frac{d\,|ClO_2^-|}{dt} = k_2\,|ClO_2^-|\,|C^*|$$

$$\log \frac{|C^*|_t}{|ClO_2^-|_t} = \log \frac{|C^*|_o}{|ClO_2^-|_o} + \frac{1}{2.3}\left(|C^*|_o - |ClO_2^-|_o\right) k_2 t$$

Cette interprétation des données des Tableaux I et II est illustrée dans la Figure V.

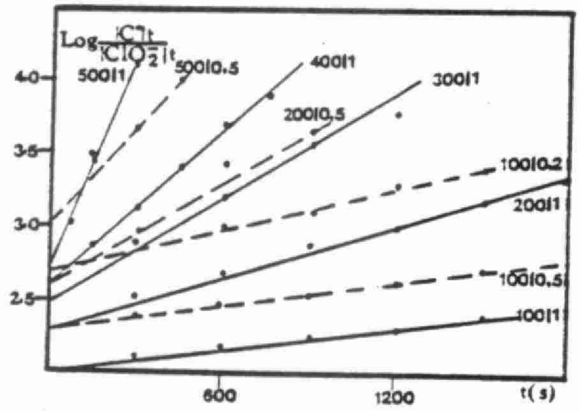

FIGURE V : Cinétique bimoléculaire charbon actif-chlorite. (Valeurs indicatives égales à $|C^*|_0 / |ClO_2^-|_0$).

Dans le calcul, nous avons accepté l'hypothèse que la «concentration en charbon actif», après un temps de réaction t, est représentée dans les équations par $|C^*|_t = |C^*|_0 - |ClO_2^-|_0 + |ClO_2^-|_t$

Il résulte de cette analyse que l'interprétation par une cinétique bimoléculaire d'ordre deux est conforme aux résultats expérimentaux. Compte tenu des données de la littérature concernant la réaction du charbon avec le chlore libre et les chloramines, il est probable qu'il y a lieu de considérer le charbon actif comme partenaire réactionnel effectif et non comme catalyseur ou adsorbant uniquement. En effet, la décomposition du chlore sur charbon donne lieu à une variété de produits réactionnels (13) comprenant notamment des produits organochlorés (12) (14), tandis que les produits de réaction inorganiques comportent des oxydes de carbone, des protons, des ions chlorure et chlorate (12, 14).

En conclusion, la réaction chlorite-charbon est, dès lors, proposée comme étant du type bimoléculaire et d'ordre deux susceptible d'apparaître comme pseudo-monomoléculaire selon les conditions expérimentales. En outre, dans le cas d'un grand excès de charbon, les mesures deviennent moins précises par suite de l'augmentation de la vitesse réactionnelle.

Un essai de saturation du charbon par un excès de chlorite (données du Talbeau III) conduit à une isotherme de Freundlich sur un large domaine de concentration. La phase d'adsorption intervient donc également dans le mécanisme. Le taux de chargement maximal obtenu s'établir à environ 0,45 g de chlorite par g de charbon.

Les données du Tableau IV indiquent que l'ion chlorite est transformé en chlorure et explicitent les quelques observations fragmentaires décrites dans la littérature (22). Nous avons donc tenu à vérifier l'effet de l'ion chlorure sur la cinétique réactionnelle en procédant par la méthode des ajouts (Tableau V).

Interprétée par l'hypothèse d'une cinétique apparente du premier ordre, la corrélation entre k_a et la concentration en chlorure est bilogarithmique (voir figure VI). L'incidence de Cl^- sur k_2 est reprise dans la Figure VII.

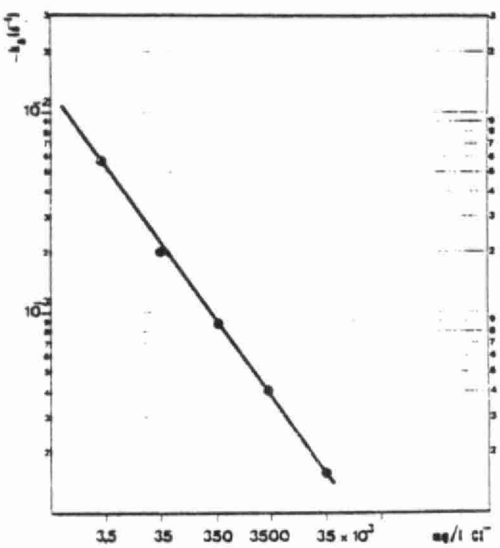

FIGURE VI : Incidence de l'ion chlorure sur la réaction chlorite-charbon actif (hypothèse de cinétique apparente du premier ordre).

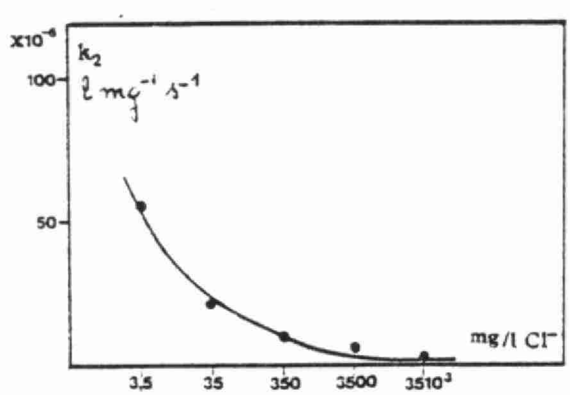

FIGURE VII : Incidence de l'ion chlorure sur la réaction chlorite-charbon actif (selon l'interprétation de la cinétique d'ordre deux).

Les deux modes d'interprétation convergent vers la même conclusion, à savoir l'importance considérable de la concentration en chlorure sur la vitesse de la réaction de l'ion chlorite avec le charbon actif. De plus, pour l'eau de surface et l'eau potable, l'incidence est surtout importante dans la gamme des concentrations usuelles. Il s'agit donc d'un facteur important dans la comparaison des résultats de différentes recherches.

Dans une expérience complémentaire, nous avons préalablement saturé le charbon par contact avec du chlorure de sodium en solution. Le charbon ainsi traité et séché avant la mise en œuvre ne montrait aucune différence de capacité et de vitesse d'élimination de l'ion chlorite par rapoort au charbon non traité. Par contre, en se basant sur le formalisme d'interprétation des mécanismes de compétition dans l'inhibition des réactions enzymatiques (25), nous observons que nos données expérimentales sont conformes à une inhibition du type compétitive entre le «substrat» chlorite et le chlorure. En effet, les droites de régression obtenues en portant l'inverse des vitesses initiales en fonction des inverses des concentrations initiales convergent, comme dans le cas de l'inhibition compétitive, vers une valeur unique de 1/v max (figure VIII). Les valeurs extrapolées de $\frac{1}{v\ max}$ sont trop proches de zéro pour permettre un calcul plus précis des éequilibres support actif-compétiteur. Nous ne citerons donc que l'ordre de grandeur de 0,2 mg/l pour la valeur de $K = \frac{|Cl^-|\,|C^*|}{|C^*|\,|Cl^-|}$ pour des concentrations suffisament élevées en chlorure, par exemple du même ordre que celles en charbon actif. A noter que la valeur de l'ordonnée à l'origine proche de zéro, voire légèrement négative, indique que d'autres paramètres que l'ion chlorure interviendraient dans la compétition (diffusion, spécificité du site, ...).

A l'usine de Tailfer, nous avons procédé à quelques essais d'orientation en dosant des concentrations contrôlées de chlorite dans l'eau brute à l'entrée des décanteurs pulsators dont le lit de boue contient du charbon actif.

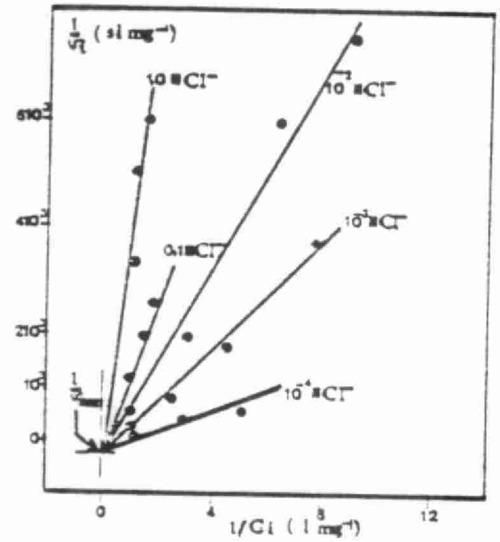

FIGURE VIII : Inhibition compétitive Cl^-/ClO_2^- dans la réaction avec le charbon actif.

Pour une durée de contact de 80 min., avec un lit de boues contenant 300 g/l de charbon NORIT W 20, la concentration en chlorures de l'eau étant de 15 mg/l, l'élimination observée était de 27,5 % pour $|ClO_2^-|_0$ = 800 mg/l et de 28,6 % pour $|ClO_2^-|_0$ = 420 mg/l. Une élimination partielle mais significative, de l'ordre de 25 à 30 %, peut donc être attendue en pratique.

Dans la conception des filtres d'adsorption sur charbon actif, la précision de la durée de service est une notion d'importance majeure. La généralisation d'essais en modèle réduit ou en unité pilote se fait souvent selon le concept d'une relation linéaire entre l'épaisseur de la couche et le temps de service (26). Celle-ci est explicitée par une droite expérimentale obtenue en portant le temps de service en fonction de l'épaisseur. En appliquant cette méthode aux courbes de percement (Figure II) pour des valeurs de ≤ 20 % de la concentration initiale, nous obtenons la courbe illustrée dans la Figure IX.

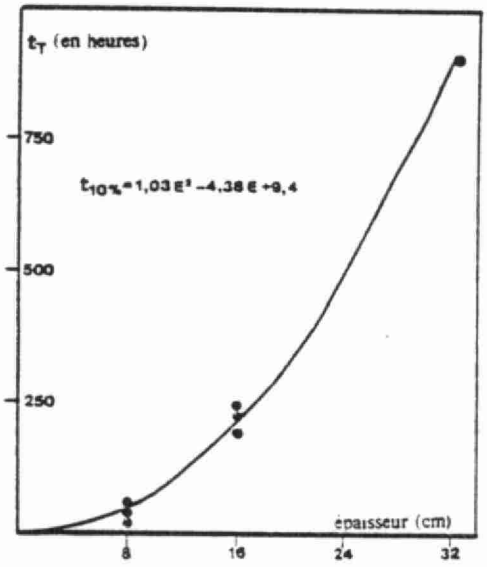

FIGURE IX : Courbe de corrélation des temps de percement par l'ion chlorite sur charbon NORIT ROW 0.8 supra.

En procédant par calcul des tangentes à la parabole expérimentale, on constate que pour 1000 h de fonctionnement, l'épaisseur minimale nécessaire est de 34 cm (E_0 = 18,5 cm) ; pour une année entière, elle serait de 94 cm (E_0 = 48,5 cm). Une épaisseur de couche de 2 m assurerait une autonomie de fonctionnement de 40.250 h ou 4 années et 7 mois. Ces extrapolations expliquent que, dans la pratique des usines, l'épuisement de la capacité de réduction du chlorite n'interviendrait qu'après celle de la capacité d'adsorption des produits organiques. Cet épuisement ne serait donc pratiquement pas observé.

CONCLUSIONS

* L'élimination de l'ion chlorite par réduction en chlorure sur charbon actif est un processus bimoléculaire d'ordre deux. Vu l'excès de charbon généralement présent, que ce soit en usine ou en laboratoire, la réaction apparaît souvent comme pseudo-monomoléculaire avec un ordre apparent de un.

* La généralisation du concept bimoléculaire pour l'élimination du chlore et des chloramines, décrite dans la littérature par un processus du premier ordre, mériterait un examen complémentaire.

* Le charbon actif possède un nombre de sites actifs lors de sa réaction avec le chlorite. Quant au charbon en poudre NORIT W 20 testé plus exhaustivement, le taux de chargement maximal s'établit à environ 0,45 g ClO_2^-/g C* soit une valeur nettement plus élevée que celle rapportée dans la littérature relative à d'autres charbons (4).

* Différents charbons soumis à un test d'orientation ont montré une vitesse de réaction différente. Le taux d'élimination du chlorite présent en grand excès par rapport au charbon peut être décrit par l'isotherme d'adsorption selon Freundlich.

* La réaction correspond à la stoechiométrie d'une réduction du chlorite en chlorure.

* Dans la pratique, l'utilisation du charbon actif en poudre, mis en œuvre dans un décanteur à lit de boue possédant un facteur de concentration de 50 à 100, réduit sensiblement la teneur en chlorite résiduel après 30 à 60 min. de temps de contact. Toutefois une interférence significative de l'ion chlorure est mise en évidence dans cette étude ; elle est conforme au mécanisme d'inhibition compétitive tel qu'il est observé quelquefois dans des réactions enzyme-substrat. La compétition de l'ion chlorure est très importante déjà pour des concentrations en chlorure inférieures à 100 mg/l, de sorte qu'elle se produira pour la plupart des eaux de surface et des eaux potables. Cet effet et l'intervention éventuelle d'autres molécules compétitives limiterait, selon les conditions particulières de chaque installation, l'élimination de l'ion chlorite au moyen de charbon actif en poudre.

* La filtration sur charbon en grain dans la pratique du traitement par adsorption conduit à des durées prévisibles d'efficacité plus longues pour l'élimination de l'ion chlorite que celles présidant à la conception des filtres d'adsorption.

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RAPPORT D'ASSEMBLÉE GÉNÉRALE

L'assemblée générale de notre Association s'est tenue le 6 Mars 1986 à 17h30 dans la Salle des Actes de la Faculté de Pharmacie de Paris.

Le rapport moral présenté par le Secrétaire Général a été adopté à l'unanimité.

Après lecture par le Trésorier et avis favorable des Commissaires aux Comptes le rapport financier a été adopté à l'unanimité.

Le dépouillement du scrutin d'élection du Conseil d'Administration a donné les résultats suivants :

– Votants :	62
– Suffrages exprimés :	62

Ont obtenu :

– Monsieur FESTY :	62 voix, élu.
– Monsieur BONTOUX :	61 voix, élu.
– Monsieur RAMBAUD :	61 voix, élu.
– Monsieur RODIER :	61 voix, élu.
– Monsieur SCHWARTZBROD :	61 voix, élu.
– Mademoiselle PEPIN :	60 voix, élue.
– Monsieur VILAGINES :	1 voix

La séance a été levée à 18 heures.

Paris, le 6 Mars 1986

Le Secrétaire Général
Le Secrétaire Général Adjoint

RAPPORT MORAL

L'année 1985 a été endeuillée par le décès de l'un de nos sympathisant les plus éminent, Monsieur le Sénateur LALLOY, auteur de l'un de nos textes de Loi les plus importants en hydrologie : La Loi sur l'eau. Au nom de notre Association je prie sa famille de bien vouloir accepter nos plus sincères condoléances.

A la suite de départs à la retraite nous avons enregistré avec regret la démission de plusieurs membres éminents : Monsieur le Professeur ALDIGHIERI, Madame GUELIN, Madame BERTRAND. Nous leur souhaitons une longue et heureuse retraite. Nous avons par ailleurs noté avec plaisir l'adhésion de 8 nouveaux membres.

En ce qui concerne notre activité scientifique nous avons tenu le 1er Mars à Paris une séance particulièrement suivie ayant trait aux problèmes de l'évolution de la qualité des eaux lors de leur stockage dans des bassins de situation.

Le 10 Mai nous avons été accueillis à TOURS où le Professeur CLANET avait organisé une séance consacrée à l'épuration des eaux par filtration.

Finalement les 10 et 11 Septembre 1985 le Professeur BLOCK a organisé une séance internationale particulièrement dense sur le thème de l'intéraction entre

PROJECT DESCRIPTION

Project Title:

OPTIMISATION OF REMOVAL OF RADIOACTIVE ISOTOPES
IN UPFLOW SLUDGE BLANKET CLARIFIERS

Contact (name of person, organization, address, telephone):

Dr. W.J. MASSCHELEIN
Director of the Laboratories
Brussels Intercommunal Waterboard
Chaussée de Waterloo 764
B - 1180 BRUSSELS
(BELGIUM)

Project Description (Please attach a schematic diagram if appropriate):

Typical radioisotopes from fall-out are removed at variable yield by conventional upflow-settling after coagulation with aluminium sulphate e.g., at maximum, 103Ru = 73 %; 58Co = 61 %; 131I = 17 %; 134CS = 38 %.

The whole process corresponds to a saturation phase of the sludge :

$$\ln \frac{A_{sat} - A}{A_{sat}} = - kt + (\text{rest})$$

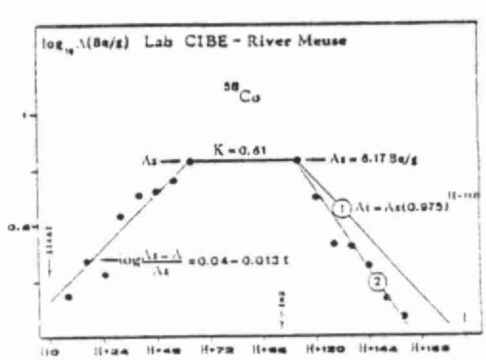
an equilibrium phase : K = Asat (Bq/g)/(V<H2O>/g) . A0(Bq/l)

and a two-stage desaturation phase both through sludge purge :

$$A_t = A_{sat}\,(1 - \text{purge})^{t - t0} \quad \text{(curve 1)}$$

and by elution of activity from the sludge into the water δ(Bq/g) = - a δt (curve 2).

<u>Typical example</u> : 58Co



Operating and cost data (including data on efficiency, results, etc.):

No extra cost compared to conventional coagulation-flocculation settling

Place(s) of installation/application (including dates):

TAILFER plant of the BRUSSELS' INTERCOMMUNAL WATERBOARD

Patent status, if applicable:

open

Other information (e.g., funding source, cooperating agencies, etc.):

If available attach descriptive publications, technical literature, manufacturers' specification, patent descriptions, etc.

EMERGING WATER SUPPLY TECHNOLOGY AWWARF Code #: BE-07

PROJECT DESCRIPTION

Project Title:

Polyurethane prefilters to improve slow sand filters

Contact (name of person, organization, address, telephone):

Prof. Dr. ir. W. Verstraete - Director
Ir. P. Vochten - Project Leader
Faculty of Agricultural Sciences
Laboratory of Microbial Ecology
Coupure L 653
B-9000 GENT Tel. (091)23.69.61 Telefax (091)23.86.28

Project Description (Please attach a schematic diagram if appropriate):

Two types of prefilters made of reticulated polyurethane to improve slow sand filters were studied. Figure 1 shows the principle of both process modifications.

In the ES (Expanded Schmutzdecke) concept, a layer of fine polyurethane is placed on top of the filter bed of a slow sand filter. The micro-organisms that grow on this highly porous matrix are spread out over a deeper layer than is the case in the sand bed of a conventional slow sand filter. In this way, the time the water is in contact with this layer with high microbial activity, is prolonged.

To avoid deterioration of the slow sand filter's filtrate, due to high loads of organic matter or NOD, an aerated prefilter of reticulated polyurethane (SAP : Submerged Aerated Prefilter) is placed in the supernatant water of the filter. On the polyurethane matrix, micro-organisms grow that aerobically biodegrade these pollutants. The biological desinfection of the water is subsequently performed by the sand bed.

Operating and cost data (including data on efficiency, results, etc.):

The first modification (ES) showed at small pilot-scale a very effective resistance of the filter to clogging by precipitation of $CaCO_3$. Under circumstances where no $CaCO_3$ precipitated, filter runs were also substantionally prolonged. The biological activity of the filter increased significantly as indicated by an almost doubling of the Δ DO. The second modification (SAP) also prolonged the length of the filter runs in a substantional way. The removal of BOD and NOD over the filter were significantly better and the filtrate was of a much higher quality with regard to number of Escherichia coli and Streptococcus faecalis present.

Place(s) of installation/application (including dates):

All experiments were performed at the Faculty of Agricultural Sciences of the State University of Ghent (Coupure L 653, B-9000 Gent) during 1987.

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

Study Centre for Water Research (S.V.W.)
Ir. J.G. Janssens
Mechelsesteenweg 64
2018 ANTWERPEN
Tel. (03)238.78.30 - Telex 32139 AWW B - Telefax (03)237.97.66

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

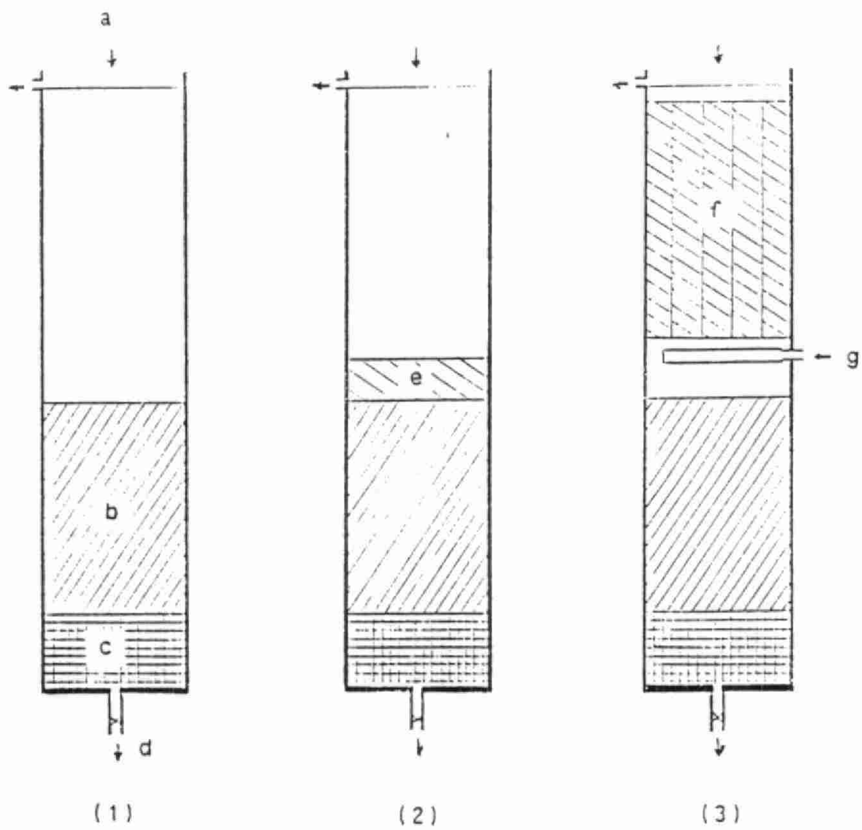


Fig. 1: Principle of polyurethane prefilters to improve slow sand filters

(1) Conventional slow sand filter
(2) Slow sand filter with ES
(3) Slow sand filter with SAP

a. raw water ; b. sand bed ; c. gravel & underdrainage ; d. filtrate ; e. layer of polyurethane ; f. polyurethane lamella ; g. aeration

CANADA

CANADA

EMERGING WATER SUPPLY TECHNOLOGY

AWWARF Code #: CA-01

PROJECT DESCRIPTION

Project Title:

Removal of Trace Organic Contaminants From Drinking Water

Contact (name of person, organization, address, telephone):

John N. Hilton
MacLaren Plansearch Inc.
2235 Sheppard Ave. E.
Willowdale, ON M2J 5A6
CANADA

Dr. Ken J. Roberts
Ontario Ministry of the Environment
1 St. Clair Avenue West
Toronto, ON M4V 1K6
CANADA

Project Description (Please attach a schematic diagram if appropriate):

This project has been undertaken to determine the following:

- the effectiveness of optimized conventional drinking water treatment for the removal of trace organic contaminants from typical Great Lakes water,
- the effectiveness of activated carbon adsorption removal of trace organic contaminants when used in the add-on contactor mode, and
- process operational parameters for the optimized operation of full scale water treatment plants and GAC adsorbers used in the add-on mode for organics removal.

The conventional treatment process (coagulation, sedimentation and filtration) chemical system was selected after an extensive series of jar tests.

The conventional process (pH 7, PACl-8 mg/L) was optimized in a state-of-the-art pilot plant (constructed of glass, teflon and stainless steel materials) and then evaluated for removal of 6 representative contaminants decachlorobiphenyl, 2,4,6-trichlorophenol, p,p'-DDT gamma-BHC naphthalene, antracene and pyrene at concentrations between 5 and 10 ug/L.

The carbon adsorption phase of the study is now underway using water from the conventional process into which 6 representative contaminants have been spiked at 100 ug/L (1,2-dichloroethane, benzene, 1,2-dichlorobenzene, tetrachloroethene, naphthalene and gamma-BHC). The residual contaminant levels are measured in each of the effluents from 3 carbon columns in series (providing cumulative EBCT's of 2 min., 10 min. and 20 min.). Also, a 20 minute EBCT has been provided to assess the removal of background contaminants.

Operating and cost data (including data on efficiency, results, etc.):

Preliminary results indicate good removal (> 90%) of decachlorobiphenyl; intermediate removal of p.p - DDT; low to intermediate removal of anthracene, pyrene and 2,4,6-trichlorophenol and, no removal to low removal of naphthalene and gamma-BHC using conventional treatment technology (coagulation, settling and filtration).

Place(s) of installation/application (including dates):

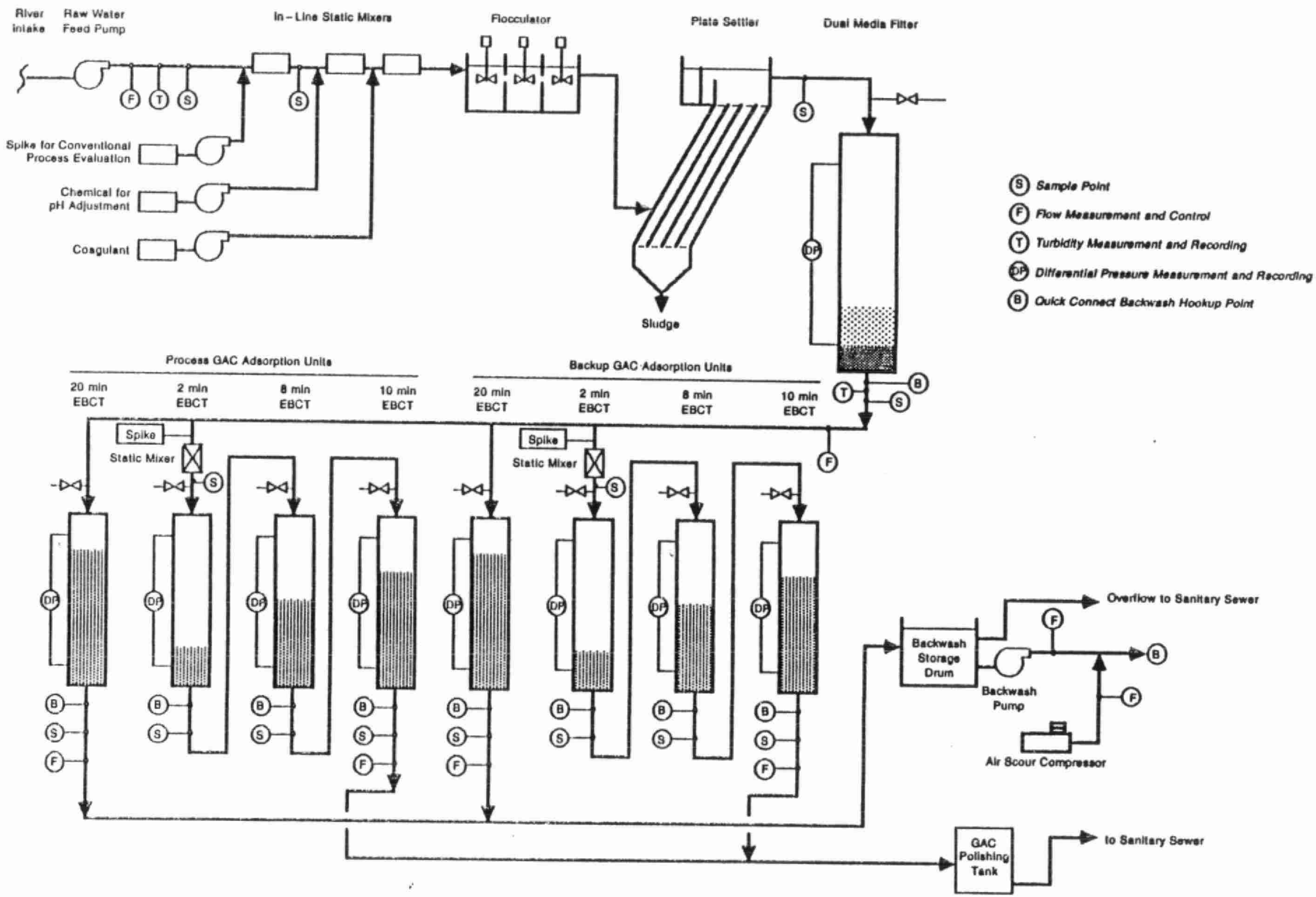
Niagara Falls, Ontario
Water Treatment Plant

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

Funded by the Ontario Ministry of the Environment

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.



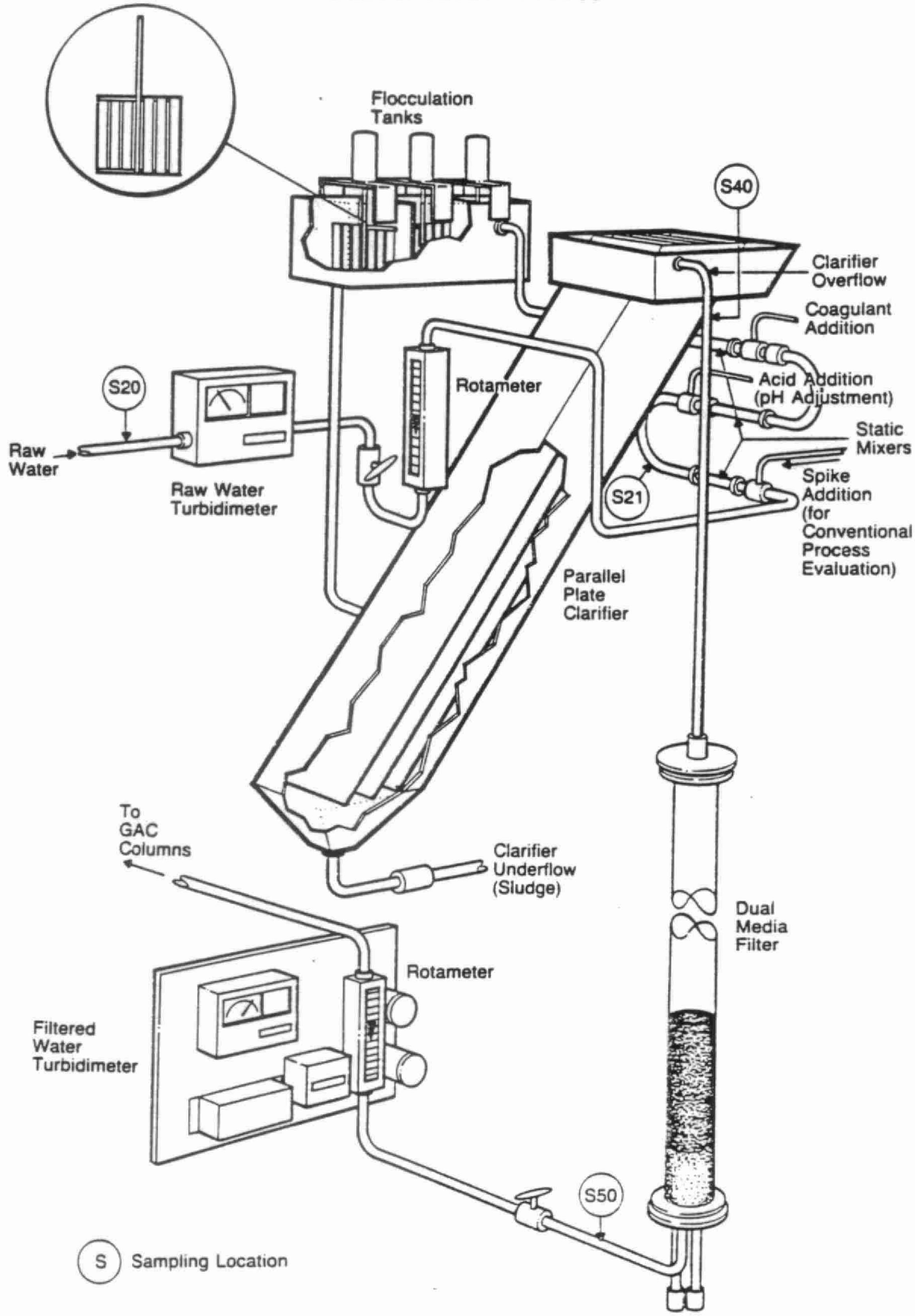
NIAGARA FALLS TRACE ORGANICS PROJECT • PILOT TREATMENT PLANT

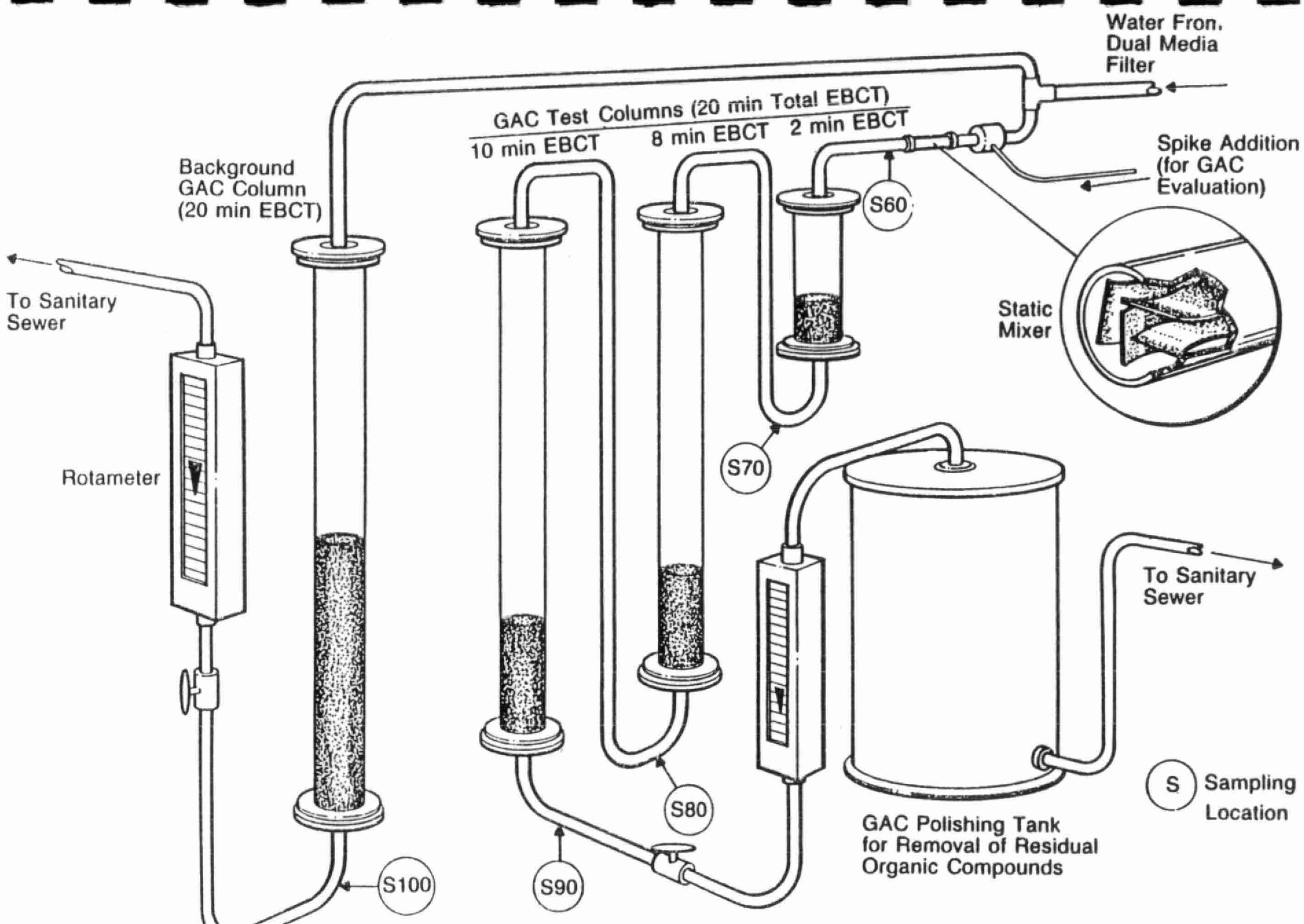
Figure 4.1

Simplified Process Flowsheet

Figure 4-2

Niagara Falls Trace Organics Project
Pilot Treatment Plant
Conventional Process





Niagara Falls Trace Organics Project
Pilot Treatment Plant
Granular Activated Carbon Process
Figure 4-3

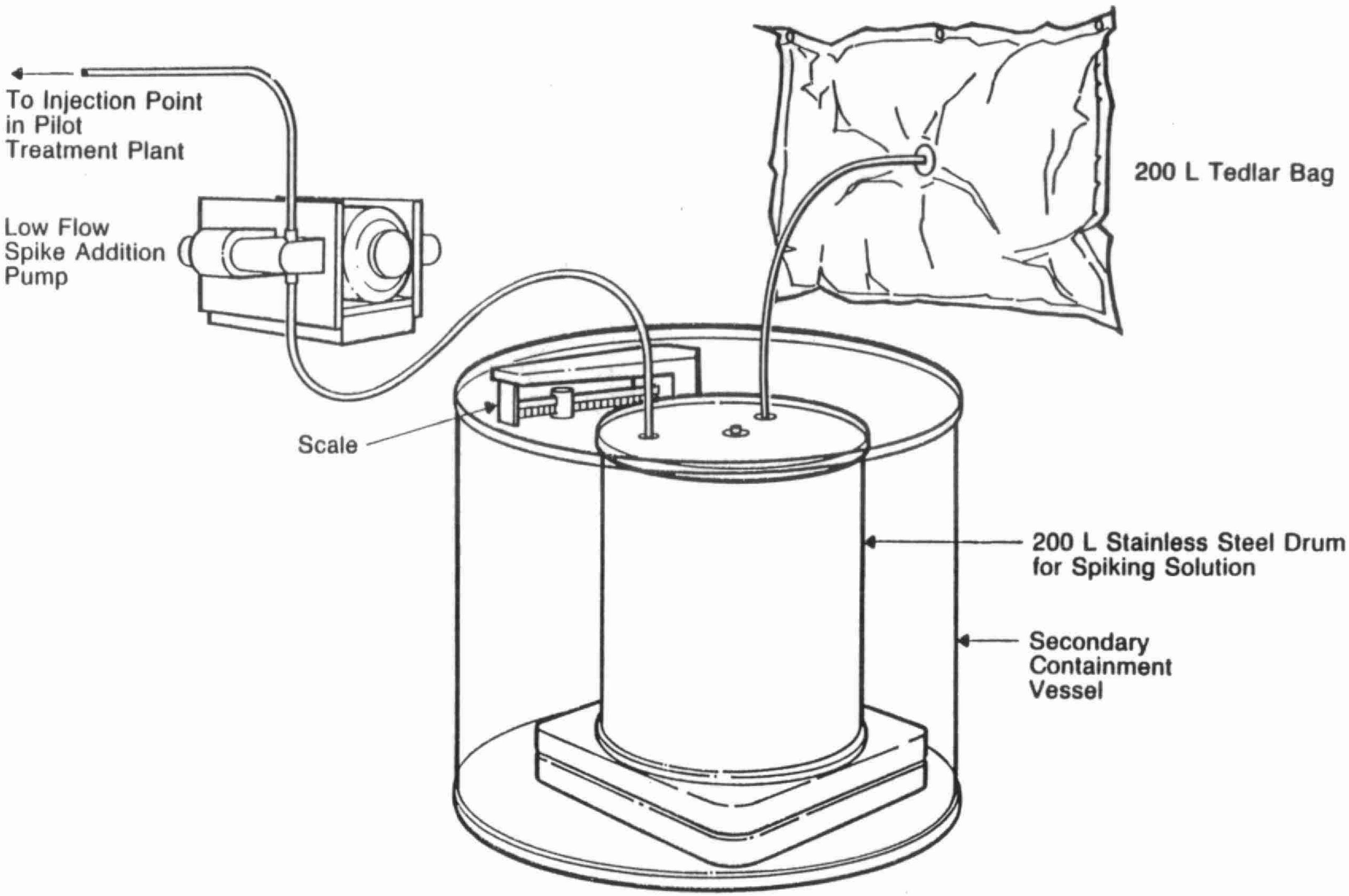


Figure 4-4

Niagara Falls Trace Organics Project
Pilot Treatment Plant
Apparatus for Storage and Addition of Spiking Compounds

PROJECT DESCRIPTION

Project Title:

Comparison of Alternative Treatment Processes for Northern Ontario Waters

Contact (name of person, organization, address, telephone):

Stuart Wyse, Ph.D., Senior Chemist or David Fisher, P.Eng., Sr. Consult.
Proctor and Redfern Limited
45 Green Belt Drive
Don Mills, Ontario M3C 3K3
CANADA

Project Description (Please attach a schematic diagram if appropriate):

Three alternative technologies were compared.

(1) Plate separators and plate flocculators from Pieklenrood,

(2) Mechanical flocculation and plate separation, and

(3) Neptune "Trident" System.

The Pielkenrood system with its plate separator and plate Flocculator has never been applied to water as found in Northern Ontario. Although it is used in Norway on waters of high colour (200TCU) and on very turbid water in other locations, this application in Canada is new. Plate separators are used in water treatment plants in Canada, however, plate flocculators have not been applied to water treatment systems in Canada. The more conventional method of flocculation using mechanical flocculators was also examined as a means of treatment of the Kirkland Lake water.

The Neptune "Trident" system incorporating a combined upflow clarifier and downflow filter system has been installed in one Ontario plant for the removal of colour and also on turbid water. However, the colour removal plant is oversized and only operates for one or two hours a day, thus a true evaluation of this system had not been performed.

This study compared the application of the three processes during the period of maximum water demand in February which was also the coldest time of the year.

Operating and cost data (including data on efficiency, results, etc.):

The ideal floc for separation by plates is large. However, the coloured floc was fragile and the Pielkenrood system with more gentle action worked much better than the mechanical flocculation. Sludge re-circulation is very necessary and adequate coagulant contact time must be provided prior to flocculation. Flocculation contact time of 10-15 minutes works well. Plate unit rise rate in the 0.50-0.80m/hr range. Gross rates in the 10m/hr plus range due to compact plates. Filter rate 9-12m/hr.

The Neptune "Trident" system relied upon the formation of a hard small floc which is removed in the upflow clarifier. This system produced good quality water with runs in excess of 24 hours using aluminum sulphate, Magnafloc 986 N, and Nalco 8105. However, the upflow clarifier in this system requires frequent backwashing in order to work effectively, in this case every eight hours. Clarifier rate of 24m/hr and filter rate of 12m/hr. No cost data available at this time.

Place(s) of installation/application (including dates):

Research was carried out at the Town of Kirkland Lake, Ontario. Field work was commenced in January 1987 and report work completed by the end of 1987.

Patent staus, if applicable:

Existing equipment systems were used - no new patents would be applicable.

Other information (e.g., funding source, cooperating agencies, etc.):

The project was funded by the Ontario Ministry of the Environment through the Research Advisory Committee.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

PLATE FLOCCULATOR & SEPARATOR RESULTS

Typical Good Result - Alum 25 mg/L, Activated Silica 1.5 mg/L

Parameter	Raw Water	Clarified Water	Filtered Water
Iron (mg/L)	.082	.310	.110
Manganese (mg/L)	.110	.040	.038
Aluminum (mg/L)	.029	1.300	.056
Zinc (mg/L)	.001	.004	.032
Sulphate (mg/L)	5.00	28.70	29.70
Turbidity (NTU)	.82	1.42	.37
Colour (TCU)	16.0	4.5	5.5
Dissolved Organic Carbon (mg/L)	7.0	3.3	3.0
Langlier's Index	-.90	-1.80	-1.60
Ion Balance Calculation (%)	156.2	179.8	180.3
Ion Balance Calc'n mg/L	74.83	87.89	87.83
Ion Balance Calc'n UMHO/CM	156.2	179.8	180.3
Conductivity 25C UMNO/CM	151.0	167.0	166.0
Hardness, Total mg/L	50.0	49.0	50.0
Alkalinity mg/L	40.8	23.8	21.2
pH	7.57	6.97	7.16
Chloride mg/L	16.70	16.10	16.70

TRIDENT SYSTEM RESULTS

Typical Good Result - Alum 8.7 mg/L, Cationic Polymer 3.5 mg/L, Non-Ionic Polymer 0.05 mg/L

Parameter	Raw Water	Clarified Water	Filtered Water
Iron (mg/L)	.024	.020	.010
Manganese (mg/L)	.011	.006	.004
Aluminum (mg/L)	.012	.370	.029
Zinc (mg/L)	.008	.012	.005
Sulphate (mg/L)	6.77	11.34	11.76
Turbidity (NTU)	.45	.63	.56
Colour (TCU)	14.0	2.5	4.5
Dissolved Organic Carbon (mg/L)	6.0	4.6	4.5
Langlier's Index		-.95	
Ion Balance Calculation (%)	.1063	5.370	4.417
Ion Balance Calc'n mg/L	74.79	90.79	91.49
Ion Balance Calc'n UMHO/CM	155.8	187.2	188.5
Conducitivity 25C	147.0	180.0	179.0
UMHO/CM	147.0	180.0	179.0
Hardness, Total mg/L	49.0	47.0	48.0
Alkalinity mg/L	39.1	36.3	37.0
pH	7.83	7.63	7.58
Chloride mg/L	16.70	25.10	24.60

PROJECT DESCRIPTION

Project Title:
Development of an Optimum System for the Application and Regulation of Powdered Activated Carbon in Water Treatment Plants.

Contact (name of person, organization, address, telephone):
Mr. F.J. Dart
Ministry of the Environment
Water Resources Branch
1 St. Clair Avenue West
Toronto, Ontario
M4V 1K6
Tel: (416) 323-4876

Project Description (Please attach a schematic diagram if appropriate):

This is a study going from laboratory bench to pilot-plant work at an operating water treatment plant aimed at enhancing the practicability of powdered activated carbon (PAC) use. Both regular or emergency requirements at potable water treatment plants will be considered. Through development of innovative or optimized pilot plant design and study, the project seeks to emphasize an ease of physical application and subsequent removal of PAC from the process stream. This goal is to be consistent with effective contaminant adsorptions and practical carbon reuse.

Operating and cost data (including data on efficiency, results, etc.):

Contract: $330,125.00 over three budget years.

Present Status: Literature search on present use of PAC and alternative reactor evaluations is completed.

Place(s) of installation/application (including dates):

Yet to be determined.

Project to be completed November/89.

Patent status, if applicable:

Contractor with Province's acquiescence may apply for rights for extra-provincial use.

Other information (e.g., funding source, cooperating agencies, etc.):

Contractor: Zenon Environmental Inc.
Burlington, Ontario

Funding: Ontario Ministry of Environment

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

EMERGING WATER SUPPLY TECHNOLOGY AWWARF Code #: CA-04

PROJECT DESCRIPTION

Project Title:

Deaeration of Oxygen Super Saturated Raw Water

Contact (name of person, organization, address, telephone):

A.P. Livingston
Associated Engineering (Ont.) Ltd.
#107, 16 Four Seasons Place
Toronto, Ontario M9B 6E5
CANADA
(416) 622-9502

Project Description (Please attach a schematic diagram if appropriate):

During the winter months, supersaturated levels of oxygen are experienced in the lake raw water feeding Buffalo Pound Water Treatment Plant. These are believed to be due to algal activity. High levels of other gases, primarily nitrogen and hydrogen sulphide are also occasionally experienced. The gases adhere to floc particles and reduce their settleability. A scum is also experienced on the clarifier surface.

Two step cascade surface deaerators are to be constructed to assist in reducing oxygen levels in the water to below saturation levels. Each deaerator has a width of 17.3m with a total, multiple stepped fall of 4.0. The design flow rate for each unit is 127000m^3/day.

Operating and cost data (including data on efficiency, results, etc.):

Operating and cost data is not available at this time.

Place(s) of installation/application (including dates):

Buffalo Pound Water Treatment Plant-Moose Jaw, Saskatchewan
Owner Cities of Regina and Moose Jaw.
Installation will be commissioned in the summer of 1988.

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

Bench scale and pilot plant research was undertaken as part of predesign engineering for the expansion of the existing plant.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

EMERGING WATER SUPPLY TECHNOLOGY

AWWARF Code #: CA-05

PROJECT DESCRIPTION

Project Title:

ELEVATION OF TREATED WATER PH BY AIR STRIPPING.

Contact (name of person, organization, address, telephone):

A.P. LIVINGSTON
ASSOCIATED ENGINEERING (ONT.) LTD.
#107, 16 FOUR SEASONS PLACE
TORONTO, ONTARIO
M9B 6E5
TEL (416) 622-9502

Project Description (Please attach a schematic diagram if appropriate):

A coarse bubble diffused air, air stripping system has been installed in the treated water clear well of the Buffalo Pound Water Treatment Plant. The system is designed to elevate the pH of the final alum-treated water from around 7.2 to 7.5, by the removal of carbon dioxide, thus reducing the need for the addition of soda ash.

The system comprises one duty and one standby multistage air blower, each of $83m^3$/min capacity coupled to a distribution and diffusion system with a total length of approximately 300m.

Potable water quality is also enhanced by the simultaneous reduction in chlorinous gas concentrations such as nitrogen trichloride.

The average plant flow is $96,000m^3$/day.

Operating and cost data (including data on efficiency, results, etc.):

Prior to installation of the system, the annual costs for the increase of pH by soda ash amounted to approximately $200,000. It is estimated that an annual saving of about $50,000 now results from the use of the air stripping system.

The saving in soda ash dose rate is between 10-15 mg/L. It is not feasible to increase the pH above 7.5 due to the alkalinity of the water, unless further soda ash is added.

Place(s) of installation/application (including dates):

Buffalo Pound Water Treatment Plant-Moose Jaw, Saskatchewan.
Owner-Cities of Regina and Moose Jaw.
Installation Completed in 1986.

Patent staus, if applicable:

None.

Other information (e.g., funding source, cooperating agencies, etc.):

Particular attention must be paid to ventilation of air space above clearwell to eliminate increase in partial pressure of CO_2 and corresponding reduction in system efficiency.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

PROJECT DESCRIPTION

Project Title:

COMBINED USE OF P.A.C. AND G.A.C. TASTE AND ODOUR REMOVAL

Contact (name of person, organization, address, telephone):

A.P. LIVINGSTON ASSOCIATED ENGINEERING (ONT.) LTD.
#107, 16 FOUR SEASONS PLACE
TORONTO, ONTARIO
M9B 6E7

TEL (416) 622-9502

Project Description (Please attach a schematic diagram if appropriate):

Operational experience with the current G.A.C. installation has shown that the system does not respond immediately to peak TOC and geosmin loadings. Up to 3 days can elapse before the G.A.C. system effectively removes peak loads. In addition, occasional short term algal blooms occur during the G.A.C. regeneration period and cause unacceptable taste and odours in the treated water.

A P.A.C. dosing system was proven, through pilot trials, to be effective in reducing the peak load on the G.A.C. contactors and to be capable of reacting to peak loads more quickly than the G.A.C. contactors.

The P.A.C. system will also be used to control short term taste and odour problems occuring during the G.A.C. winter regeneration period.

Operating and cost data (including data on efficiency, results, etc.):

Pilot finals indicate a P.A.C. dose of about 15 mg/L will achieve a reduction of the TOC loading of about 10%, and a 50% reduction in the geosmin level reaching the contactors.

Cost data is not yet available.

Place(s) of installation/application (including dates):

Buffalo Pound Water Treatment Plant-Moose Jaw, Saskatchewan.
Owner-Cities of Regina and Moose Jaw.
System will be commissioned in 1989.

Patent staus, if applicable:

None.

Other information (e.g., funding source, cooperating agencies, etc.):

Pilot plant research was undertaken as part of the predesign engineering for the expansion of the existing plant.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

EMERGING WATER SUPPLY TECHNOLOGY AWWARF Code #: CA-07

PROJECT DESCRIPTION

Project Title:

Magnetometer Surveys for Groundwater Exploration

Contact (name of person, organization, address, telephone):

Laurent Letendre/Scotte Greene
Hydrogeo Canada Inc.
1100, Dorchester Blvd. West
Montreal, Quebec H3B 4P3
CANADA
(514) 866-2601

Project Description (Please attach a schematic diagram if appropriate):

A portable magnetometer records the magnetic field intensity along grid profiles. The data is processed by computer and interpreted, by Hydrogeo Canada, Inc., based upon a contoured map of the magnetic field intensity within the study area. The varying intensity is interpreted to be an indication of thickness of overburden.

This interpretation makes the magnetometer a particularly useful tool in selecting drilling locations in alluvial deposits. The magnetometer has also been useful in identifying fractures and faults (of interest in de-contamination projects). Magnetometer surveys could be followed by conventional resistivity profiles in selected areas to locate thick overburden materials of suitable permeability for drilling of exploratory and production boreholes.

Operating and cost data (including data on efficiency, results, etc.):

About $800 per day including instrument use and professional fees, plus field expenses (travel and accommodation).

Office data processing and interpretation is also $800 per day.

Place(s) of installation/application (including dates):

Used for a confidential client in Eastern Townships, Quebec to determine location of fractures in which contaminated groundwater may move. Used to locate possible fractures in Miron Quarry, Montreal, in order to evaluate its suitability as a landfill site. (7-11 Nov, 1987). Used also in locating suitable drill sites for the supply of water to the Wemindji Band, James Bay Territory, Quebec (Oct. 9th - Dec 12, 1987). Used extensively in granite areas of West Africa to locate favorable water well drilling locations.

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

EMERGING WATER SUPPLY TECHNOLOGY

AWWARF Code #: CA-08

PROJECT DESCRIPTION

Project Title:

Hydrocarbon leak detection using radon

Contact (name of person, organization, address, telephone):

Laurent Letendre/Scott Greene (514) 866-2601
Hydrogeo Canada Inc.
1100 Dorchester Blvd West
Montreal, Quebec
H3B 4P3

Project Description (Please attach a schematic diagram if appropriate):

Radon gas is an inert, radioactive element known to be associated with hydrocarbons. The radon gas rises to the surface from subsurface hydrocarbons by way of diffusion and is enhanced by methane migration to the surface. Thus in locations where hydrocarbons exist at depth, radon gas will be present within the soil horizons at the surface.

A radon detector is used to measure gamma radiation emitted by the $Radon_{222}$ isotope in the air within the soil horizons. Numerous air samples are taken about the study area at a constant depth. Corrections are made for background radiation levels. The data processing produces a map of the relative distribution of $radon_{222}$ over the study area and thus a plan view of the distribution of hydrocarbon in the subsurface. This is an essential first step in the clean up of hydrocarbon spills. Concentrations are registeres in the memory of the instrument, and are dumped later into a computer for processing. The computer analyses the data using our own software and plots a map of concentrations. The map inables the user to identify immeidately those areas where rehabilitation is needed, prior to installation of piezometers and recovery wells. Thus the source location of the spill is immediately apparent and can be treated from the outset.

Operating and cost data (including data on efficiency, results, etc.):

Each investigation is unique, so spacing for data points and the number required are variable. Generally 5 or 6 days field and office work are required, at a cost of about $600 per day plus travel expenses.

Place(s) of installation/application (including dates):

Most clients for this type of work prefer confidentiality. However, the system has been used with success in several rural and urban settings (gas station, schools, industries) in Quebec and Nova Scotia.

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

The final report on each radon survey includes recommendations on how to carry out the cleanup of the spill, work which is also done by Hydrogeo Canada, Inc. Repeated surveys during a cleanup can serve to monitor the effectiveness of the cleanup.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

EMERGING WATER SUPPLY TECHNOLOGY

AWWARF Code #: CA-09

PROJECT DESCRIPTION

Project Title:

Pilot Plant Assessment of Coagulation and Filtration Strategies for Treatment of Cold, Low Turbidity Waters

Contact (name of person, organization, address, telephone):

Dr. Erika E. Hargesheimer
Glenmore Waterworks Laboratory (35)
P.O. Box 2100
Calgary, Alberta T2P 2M5
CANADA

Project Description (Please attach a schematic diagram if appropriate):

The effectiveness of low temperature (1 - 3°C) drinking water treatment with chemical coagulants and filtration aids is being investigated. The two year study began in the winter of 1986 and will be completed in March, 1988. The cold water coagulation studies are being conducted firstly at bench scale followed by pilot plant scale and ultimately at full drinking water treatment plant scale. The effects of chemical addition on a number of finished water quality parameters (pH, saturation index and aggressiveness, turbidity, particle size distribution, bacterial counts, zeta potential, aluminum concentration) and on treatment plant operations (filter bed performance, backwash frequency) are being studied.

Operating and cost data (including data on efficiency, results, etc.):

Estimated Project Operating Costs: $50,000

Place(s) of installation/application (including dates):

Glenmore Water Treatment Plant and Bearspaw Water Treatment Plant
Calgary, Alberta, Canada T2P 2M5
The City of Calgary
Engineering Dept., Waterworks Division
P.O. Box 2100, Calgary, Alberta T2P 2M5
CANADA

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

See enclosed report

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

PRELIMINARY FINDINGS OF FILTRATION STUDY

PART 1. EXECUTIVE SUMMARY

WATERWORKS DIVISION
ENGINEERING DEPARTMENT
THE CITY OF CALGARY
JULY 22, 1987

1. BACKGROUND

At both the Glenmore (GWTP) and Bearspaw (BWTP) Water Treatment Plants, chemical coagulation has been historically practiced only during high turbidity periods associated with spring runoff. During the rest of the year, the current Federal guideline turbidity objective of 1 NTU can be easily achieved without the use of alum or polyelectrolyte. The provincial Licence to Operate has not in the past required chemical coagulation as a mandatory treatment practice.

Recently, however, studies have reported that Giardia cysts, bacteria and other microbiological organisms may pass through the filters. Chlorine resistant organisms in these size ranges could, therefore, be present even though the finished water turbidity is well below the 1 NTU drinking water standard. The use of chemical coagulation would, perhaps, reduce the potential for break-through of these organisms. Very little specific information is available in the literature regarding the effectiveness of coagulant and filter aids under the cold water (1 - 3°C) low turbidity conditions typical of both GWTP and BWTP source water. Thus in 1986, Alberta Environment requested that Waterworks Division explore the feasibility of year-round chemical coagulation.

2. APPROACH

The Waterworks Division undertook a preliminary series of low temperature (1 - 3°C) tests from December 1986 to March 1987. The cold water coagulation studies were conducted firstly at bench scale followed by pilot plant scale and ultimately at plant scale. The program of studies endeavored to accommodate existing plant constraints at GWTP and BWTP summarized in Table 1 and Table 2, respectively. The effects of chemical addition on a number of finished water quality parameters (pH, saturation index and aggressiveness, turbidity, bacterial counts, zeta potential, aluminum concentration) and on treatment plant operations (filter bed performance, backwash frequency) were studied.

3. KEY FINDINGS

Findings detailed below for ferric sulphate, polyelectrolyte and alum are summarized in Table 3.

a) FERRIC SULPHATE

OBSERVATIONS:

- Performed very well as a flocculant in both bench scale and pilot scale studies. Produced a settleable floc under conditions and dose rates at which alum performed poorly.
- Formed a voluminous brown floc. Sludge disposal would likely require construction of facilities for dewatering and removal by hauling.

-Effected pH depression and increased finished water aggressiveness to an even greater extent than corresponding doses of alum.
-Finished water aluminum concentration unaffected by ferric coagulant. Aluminum levels remained at 20 - 40 ug/L.

CONCLUSIONS:
-More expensive, anticipated problems with sludge disposal and substantial alteration in water aggressiveness even at 5-10 mg/L doses.
-Full scale application is not recommended and investigation of this coagulant will be discontinued.

b) POLYELECTROLYTE (Cat Floc-T).

OBSERVATIONS:
-Effective in pilot plant applications as a primary coagulant.
-Improved turbidity removal while leaving aggressiveness and pH of finished water unchanged. (See Table 3).
-Proved unsuitable at BWTP as a primary coagulant for treatment of turbidities above 1 NTU.

CONCLUSIONS:
-Recommend further study of polyelectrolyte as filter conditioner, coagulant and coagulant aid to minimize dose required. (Investigate plant scale polyelectrolyte coagulation at turbidities less than 1 NTU).
-May not be significantly more expensive than alum if doses are optimized.
-Advantages of no pH alteration, no effect on finished water aluminum concentrations or aggressiveness and no major sludge disposal problems.
-Additional chemical costs estimated to range up to $175,000 annually for 0.5 mg/L dosing at both plants.

c) ALUM

OBSERVATIONS:
-Settleable floc did not form with alum doses of 5-10 mg/l under cold water (1 - 3 ^{o}C) low turbidity winter conditions.
-Filters effectively retained the colloidal floc.
-Consequences of alum doses of 5-10 mg/L in plant scale experiments at both GWTP and BWTP are summarized in Table 4.

CONCLUSIONS:
-Effects of cold water chemical dosing at BWTP and GWTP differ substantially. One plant cannot be used as a "model" to predict dose and response at the other treatment facility.
-Possible to achieve a lower turbidity than the present goal of 0.5 NTU using 5-10 mg/L cold water alum addition. Minor changes in dose, however, adversely affect plant performance as well as finished water quality.
-Cold water alum dosing affects water aggressiveness at a critical time and may result in corrosion by-products (metals) and bacteria sloughing off distribution lines into finished water.

-Additional chemical costs estimated to range up to $125,000 annually for 5 mg/L dosing at both plants.
-An alum dose of 10 mg/L increased aluminum concentrations from 40 ug/L in raw water to almost 250 ug/L in finished water. Although presently there is no water quality standard for aluminum, strict control of aluminum concentrations is warranted according to available toxicity data reported in the scientific literature. The American Water Works Association has considered setting an operating goal of 200 mg/L aluminum in finished water.

4. CONCLUSIONS

Gains in low temperature turbidity removals were achieved by using alum coagulation in pilot as well as full plant scale tests. While a 5 mg/l alum dose at GWTP resulted in improved removal of particulates in the size range of microorganisms, it may not be the best chemical for cold water pretreatment. Potential adverse effects of cold water alum addition and some operational difficulties were noted when compared to other chemical pretreatment alternatives (See Table 4). Although these preliminary study findings show promising results for chemical addition at both plants under winter conditions, further studies are required to investigate coagulants other than alum and to optimize treatment processes.

5. RECOMMENDATIONS

In order to complete investigation of yet unanswered questions and explore alternatives to alum, studies should continue in the winter of 1987-88. To accommodate these studies, it is recommended that chemical pretreatment not be a strict operational criteria in the upcoming winter season. This would allow study of dose rates, optimization of chemical application point and further study of alternative pretreatment chemicals. Some experiments would have to be carried out on uncoagulated water for comparison purposes. Therefore, periods without chemical pretreatment should be allowed in the upcoming 1987-88 winter season. The present 0.5 NTU finished water turbidity goal would allow the necessary flexibility for these continued cold water coagulation and filtration optimization studies. The following points remain to be addressed:

a) What are the actual particle sizes associated with each turbidity achieved? Are Giardia cyst size ranges effectively removed?
b) Are there efficient chemical pretreatment alternatives to alum?
c) What are the actual effects of altered water aggressiveness on finished water quality in the distribution system?
d) What chemical dosing regimes are most effective for BWTP and GWTP?
e) What analytical techniques can be used to precisely control chemical doses?

TABLE 1. Glenmore Water Treatment Plant Constraints Affecting Filtration.

CONSTRAINT	EFFECT
No filter to waste option	Higher turbidity (exceeding 0.5 NTU) water produced immediately after a backwash cannot be discarded. Clearwell water turbidity usually exceeds typical filtered water turbidity
No common injection point (i.e. influent header) to add polyelectrolyte	Polyelectrolyte is added at filter influent weirs, reducing effective mixing and contact time
No injection point for polyelectrolyte addition as a coagulant	Polyelectrolyte has historically been restricted to filter aid use.
Chemical mixing, flocculation depends on hydraulic gradient	Acceptable at high flows, but low energy input at low flows.

TABLE 2. Bearspaw Water Treatment Plant Stage I Constraints Affecting Filtration

CONSTRAINT	EFFECT
Filter "strainers" instead of underdrains	Less efficient use of media, channeling
Baffle system in backwash	Uneven distribution of air scour and backwash water
Oversized filter control valves	Flow cycling

TABLE 3. Affects of cold water chemical addition on finished water quality.

COAGULANT	% Turbidity Reduction	% Bacteria Reduction	Aggressiveness Shift	Aluminum (ug/L)
NONE	20 - 50	65	none	20 - 40
ALUM (5-10 mg/L)	70 - 85	85	increase	100 - 250
FERRIC* SULPHATE (5-10 mg/L)	70 - 85	**	marked increase	20 - 40
POLYELECTRO-* LYTE(5 mg/L)	70 - 85	**	none	20 - 40

* Pilot Plant application
** Not measured

TABLE 4. Advantages and disadvantages of 5-10 mg/L alum dosing at GWTP and BWTP.

ADVANTAGES	DISADVANTAGES
i) Turbidity approximately half that without chemical pretreatment	i) Measurable reductions in pH so that saturation index is altered during the seasonal low period to a more aggressive state
ii) Filtration efficiency for bacteria removal improved from 65% without chemical pretreatment to greater than 85%	ii) Increased finished water aluminum concentration from 100 ug/L at 5 mg/L dose to over 220 ug/L at 10 mg/L alum dose
	iii) With increased bed run time, filters become less effective at removal of aluminum
	iv) Alum dosed at 10 mg/L caused marked filter bed instability with brief durations of 0.8 NTU filtered water turbidity
	v) More frequent backwashes, more alum sludge for disposal
	vi) Difficult to set optimum dose
	vii) Added chemical costs of approximately $125,000 for alum dosed at 5 mg/L

PROJECT DESCRIPTION

Project Title:

Continuous monitoring system for toxic spills in raw water supply.

Contact (name of person, organization, address, telephone):

Dr. R. T. Seidner
The City of Calgary
Glenmore Waterworks Laboratory (35)
P. O. Box 2100
Calgary, Alberta

Project Description (Please attach a schematic diagram if appropriate):

To develop and operate a continuous monitoring system for the deleterious material in the surface water supply. The system is to be capable of distinguishing shock loads of toxic and/or bulk chemicals from normal environmental variations in parameters. The system is to be interfaced with the operating SCADA computer.

The continuous monitoring system acquires measurements of conductivity, temperature, pH, dissolved oxygen, turbidity and fish swimming behaviour. Various models of the real time data are being assessed as to capability to generate alarms to the operating SCADA computer.

Fish swimming behavior is grouped on a day/night basis.

EMERGING WATER SUPPLY TECHNOLOGY   AWWARF Code #: CA-11

PROJECT DESCRIPTION

Project Title:

Investigation of Indicator Bacteria in the City of Calgary Water Distribution System

Contact (name of person, organization, address, telephone):

Dr. Erika E. Hargesheimer
Glemore Waterworks Laboratory
P.O. Box 2100
Calgary, Alberta T2P 2M5
CANADA

Project Description (Please attach a schematic diagram if appropriate):

PROJECT OBJECTIVES:

1) Identify sources and nature of coliform bacterial populations in the City of Calgary treated water supply.

2) Assess biofilm development and stability of deposited biofilm in piping and on plumbing devices.

3) Conduct special tests to enumerate general bacterial populations, speciate and profile total coliforms, enhance the recovery of injured coliforms and provide rapid identification of *E. coli*.

4) Evaluate significance of recovered organisms.

An in-depth survey of bacterial populations is planned to supplement the routine microbiological monitoring program. Samples will be collected from more environments, more frequently and in larger volume. A broad spectrum of specific tests will be conducted on these extensive samplings to better characterize the source and nature of coliform organisms in water throughout the treatment plants as well as drinking water in the City of Calgary distribution network.

PROJECT STATUS: The research plan has been formulated and a proposal for funding has been submitted. Pending the successful granting of requested funding, the project will be conducted over a two year period beginning in June, 1988.

Operating and cost data (including data on efficiency, results, etc.):

Project Operating Costs: $203,000.00 over two years.
(Funding support requested from Alberta Environment, $118,000).

Place(s) of installation/application (including dates):

Glenmore Waterworks Laboratory (35)
City of Calgary
Engineering Dept. Waterworks Division
P.O. Box 2100
Calgary, Alberta T2P 2M5
CANADA

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

Funding Source: Alberta Environment

Cooperating Agency: City of Calgary Health Service

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

EMERGING WATER SUPPLY TECHNOLOGY AWWARF Code #: CA-12

PROJECT DESCRIPTION

Project Title:

Evaluation of Coliphage Virus Enumeration as a Surrogate Indicator of Human Enteric Viruses in Alberta Surface Waters and Treated Drinking Waters.

Contact (name of person, organization, address, telephone):

Dr. Erika E. Hargesheimer
Glenmore Waterworks Laboratory (35)
P.O. Box 2100
Calgary, Alberta T2P 2M5
CANADA

Project Description (Please attach a schematic diagram if appropriate):

One year term project in progress (Completion date, July, 1987). Results and final report available by December, 1987.

PROJECT OBJECTIVES:

1) To determine the frequency of coliphage and enteric virus isolation in surface and treated drinking water in Alberta and to assess the need for routine monitoring programs in municipal drinking water treatment plants.

2) To examine the usefulness of coliphage monitoring as a surrogate for human virus monitoring by investigating the correlation between the incidence of the two virus types.

3) To evaluate the efficiency of three Alberta drinking water treatment plants in eliminating fecal indicator bacteria, enteric viruses and coliphages and to determine the correlation between viruses and standard water quality monitoring techniques.

Surface water samples will be collected before and after treated sewage and urban runoff input from Calgary and Edmonton. Samples will be collected throughout the processes of three drinking water treatment plants. Analysis of sewage effluent samples will serve as positive controls and will also be used to further explore the correlation between the incidence of coliphage and enteric viruses. In order to assess the need for routine examination of raw and finished water samples for viruses, their occurrence will be correlated with standard water quality tests. Water samples will be analyzed for coliphages, enteric viruses, simple microbial indicators (Heterotrophic Plate Count, total and fecal coliform bacteria) and simple chemical parameters (turbidity and chlorine residual).

Operating and cost data (including data on efficiency, results, etc.):

Project Operating Costs: $50,000 ($37,700 provided by the Alberta Environmental Research Trust adn remaining funds as well as project support staff provided by the City of Calgary).

Place(s) of installation/application (including dates):

Glenmore Waterworks Laboratory (35)
City of Calgary
Engineering Dept. Waterworks Division
P.O. Box 2100
Calgary, Alberta

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

PROJECT DESCRIPTION

Project Title:

Incidence of Legionella, Aeromonas and Campylobacter in Municipal Source and Treated Drinking Water

Contact (name of person, organization, address, telephone):

Dr. Erika E. Hargesheimer
Glenmore Waterworks Laboratory (35)
P.O. Box 2100
Calgary, Alberta T2P 2M5
CANADA

Project Description (Please attach a schematic diagram if appropriate):

Sample collection and analysis for the two year project are complete and a final report is currently in preparation. Over 300 samples were analyzed for Aeromonas, Campylobacter and Legionella. The original one year project was extended and the objectives of the final one year of the project (October, 1986 - November, 1987) were:

1) To complete investigation of seasonal variation of the opportunistic pathogens Aeromonas, Campylobacter and Legionella in the source water supplies for the City of Calgary through lake turnover (May) and spring runoff 1987 (June - July)

2) To pinpoint the source of detected Aeromonas and Campylobacter by expanded reservoir, river and storm sewer monitoring. To expand the Legionella sampling network to include public building air conditioning systems, hot water tanks and boilers.

3) To correlate the incidence of these organisms to standard water quality monitoring techniques of Heterotrophic Plate Count and Total/Fecal coliforms.

4) To complete study report and assessment of findings.

Operating and cost data (including data on efficiency, results, etc.):

Project Operating Costs: $45,000.00 over two years.
Funds provided by the Alberta Environmental Research Trust

Place(s) of installation/application (including dates):

Glenmore Waterworks Laboratory (35)
City of Calgary
Engineering Dept. Waterworks Div.
P.O. Box 2100
Calgary, Alberta T2P 2M5
CANADA

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

Funding Source: Alberta Environmental Research Trust

Cooperating Agency: Mount Royal College, Calgary, Alberta

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

PROJECT DESCRIPTION

Project Title:

Artificial Recharge of Treated River Water

Contact (name of person, organization, address, telephone):

Gary J. Komar, P.Eng.
M.M. Dillon Limited
P.O. Box 1850, Station A
Willowdale, Ontario
M2N 6H5 (416) 229-4646

Project Description (Please attach a schematic diagram if appropriate):

In the mid-1970's the cities of Waterloo, Kitchener and Cambridge in Ontario were faced with the problem that municipal water demands were growing so rapidly that existing groundwater resources would be soon fully utilized. The Regional Government undertook a number of investigations over the past 10 years; these included:

- new groundwater supplies;
- a Great Lakes pipeline;
- a local surface source - the Grand River.

The ultimately decided on system was that of artificial recharge. The Mannheim artificial recharge scheme uses the storage capacity of a dry sand/gravel formation as an underground reservoir to overcome seasonal flow fluctuations of the recharge source (the Grand River). Prototype testing of the injection wells and recharge basins is planned for the next 5-8 years and the recharge scheme should be operational by the year 2001. Until this time, the cities will be supplementarily supplied directly with treated water from the Grand River. The requirement for the recharge scheme was predicated on two factors:

- the desire of consumers to continue with "groundwater" (stable temperature);
- the need to maximize the supply capability of the Grand River source.

Operating and cost data (including data on efficiency, results, etc.):

Data will not be available until prototype testing is completed.

Place(s) of installation/application (including dates):

Prototype testing of artificial recharge wells and basins will take place in Kitchener, Ontario, over the next 5 to 8 years.

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

The Region of Waterloo will provide the funding for development of the artificial recharge works.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

THE REGIONAL MUNICIPALITY OF WATERLOO
MANNHEIM ARTIFICIAL RECHARGE SCHEME

The Cities of Waterloo, Kitchener and Cambridge are unique in Canada because together they make up the largest metropolitan area in the country solely using ground water for their source of water supply. The three cities have a present total population of about 275,000. They have common municipal boundaries and are located in Southwestern Ontario in the Great Lakes Region, about 65 kilometres from the nearest lake, Lake Ontario.

In the mid 1970's, the three cities were faced with a potentially serious problem - municipal water demands were growing at such a rate that available ground water supplies, primarily within city boundaries, would be fully utilized within the not too distant future. Confronted with this problem, the Region of Waterloo, which is responsible for the water supply to the three cities, undertook a number of investigations over the past 10 years looking for a new source of water supply. Some of the potential sources that were evaluated include new ground water supplies in the rural areas surrounding the three cities, a Great Lakes pipeline, and a local surface source - the Grand River. The Grand River could be used as a direct supply of treated water or as a source for an artificial recharge scheme.

The water supply scheme that was ultimately chosen is referred to as the Mannheim Artificial Recharge Scheme. The recharge scheme should be operational by 2001. Prototype testing of injection wells and recharge basins is planned over the next 5 to 8 years.

The Mannheim Artificial Recharge Scheme uses the storage capacity of a dry sand/gravel formation as an underground reservoir to overcome seasonal flow fluctuations of the Grand River. The Mannheim Scheme is centred on the top of a moraine in an aban-

doned gravel pit located in West Kitchener, about 8 kilometres from the Grand River source. Raw river water would be pumped up to the Mannheim site, where it would be pretreated and artificially recharged using either recharge basins or injection wells. There is approximately 40 m of dry formation that now sits between the bottom of the gravel pit and the regional water table. There is the capability of storing 11.5 million m^3 of recharged water in the dry formation, enough water to supply the three cities for six months based on predicted average day demands in the year 2016. The recharged surface water would be recovered by a recovery well ring located around the recharge site.

The artificial recharge scheme maximizes the supply capability of the Grand River by abstracting more surface water in the spring and fall seasons when streamflows are above average, and taking less water in the summer and winter when river flows are low. The spring and fall abstractions are stored in the underground reservoir until needed during summer peak demands.

A secondary benefit of the artificial recharge scheme is that the seasonal quality fluctuations of the surface water are eliminated when the recharge water is stored in the ground. The consumers of the three cities are accustomed to a hard, constant temperature (10^{o}C), untreated ground water supply. Artificial recharge would make the softer, warm to cold (23^{o}C in the summer months and 2^{o}C in the winter months) pretreated surface water similar to ground water quality through movement and detention in the underground reservoir.

Until the artificial recharge works are operational in 2001, the cities will be supplied directly with treated water from the Grand River.

PROJECT DESCRIPTION

Project Title:

Process Optimization for Biological Treatment of Drinking Water

Contact (name of person, organization, address, telephone):

Dr. P.M. Huck
Department of Civil Engineering
University of Alberta
Edmonton, Alberta
T6G 2G7
Tel. (403) 432-4738

Co-investigators:
Dr. P.M. Fedorak, Microbiology
Dr. D.W. Smith, Civil Engineering, University of Alberta
Dr. D.T. Williams, Health and Welfare Canada

Project Description (Please attach a schematic diagram if app-:priate):

Drinking water treatment in North America relies almost exclusively on chemical and physical processes and seeks to avoid any microbiological activity in the treatment plant. In contrast, advanced European practice encourages microbiological activity, particularly through the use of ozone and granular activated carbon (GAC). Biological processes offer a number of advantages including lower disinfectant dosages and therefore a reduction in the formation of harmful organic byproducts.

Considerable process investigation must be done before biological processes could be successfully introduced into Canadian drinking water treatment practice. Of particular importance is the impact of ozone, which significantly increases the concentration of easily biodegradable or assimilable organic carbon (AOC). This can lead to significant bacterial regrowth problems in the distribution system.

Although methods have recently been developed in Europe to quantify AOC and the associated regrowth, they have not been used to optimize biological treatment. The objectives of the project are:

1. to evaluate, for one of the typical surface water types used for drinking water preparation in Canada, the extent to which biological treatment can reduce the level of disinfectant required, and the associated byproduct formation,
2. to determine, over a complete annual cycle, the range of process conditions capable of producing substantial removals of both total and assimilable organic carbon, with acceptable levels of bacterial biomass in the process effluent,
3. to establish whether a biologically stable water can be produced following ozonation, without GAC,
4. to quantify the impact of improved turbidity removals on the biological stability of the final water,
5. to model mathematically biodegradation in filters and biodegradation / adsorption in GAC contactors as an aid in interpreting and extending the experimental results, and
6. to transfer the study information to the consulting and municipal sectors and to government regulatory bodies.

Operating and cost data (including data on efficiency, results, etc.):

Not yet available. Project commenced in November 1987.

Place(s) of installation/application (including dates):

Research will be conducted using a previously constructed pilot plant located at the City of Edmonton's Rossdale Drinking Water Treatment plant. See project entitled "Evaluation of Alternative Drinking Water Treatment Processes at Pilot Scale by Means of Mutagenicity Testing" for more details.

Patent staus, if applicable:

N/A

Other information (e.g., funding source, cooperating agencies, etc.):

The project is funded by the Natural Sciences and Engineering Research Council of Canada (NSERC) Strategic Grants Program. Funding for operations (1987-89) is $370,426, while funding for additional equipment was also provided ($65,696). The pilot plant was constructed for a previous study funded largely by Health and Welfare Canada. Representatives of the municipal and government sectors will be involved in the project. Technology transfer seminars are planned to further disseminate the results.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

PROJECT DESCRIPTION

Project Title:

Evaluation of Alternative Drinking Water Treatment Processes at Pilot Scale by Means of Mutagenicity Testing

Contact (name of person, organization, address, telephone):

Dr. P.M. Huck
Department of Civil Engineering
University of Alberta
Edmonton, Alberta
T6G 2G7
Tel. (403) 432-4738

Co-investigator:
Dr. D.T. Williams
Health and Welfare Canada

Project Description (Please attach a schematic diagram if appropriate):

The objective of the project is to examine alternative drinking water treatment processes at pilot scale using mutagenicity testing. Mutagenicity testing using bacteria is a screening procedure which is capable of giving qualitative information on carcinogenic risk.

The specific research objectives are:

1. to examine alternative treatment processes, particularly different combinations of oxidants;
2. to monitor the breakthrough of mutagenicity on granular activated carbon and quantify the removal capability of GAC for mutagenicity;
3. to assess a yeast assay which may be more sensitive than the commonly used Ames Salmonella mutagenicity test; and,
4. to attempt to make correlations between mutagenicity and other surrogate parameters such as trihalomethanes, TOX and UV absorbance.

The study is being carried out by operating different oxidants, each followed by granular activated carbon, in parallel in a pilot plant. Using sampling points after each process step, samples are concentrated on XAD-2 resin for mutagenicity screening in parallel with GC and GC/MS analyses.

The project is expected to provide significant quantitative information concerning the formation and reduction of mutagenicity in drinking water treatment and its relation to other parameters. This will assist in providing a more comprehensive evaluation of alternative drinking water treatment processes than chemical testing alone.

Operating and cost data (including data on efficiency, results, etc.):

Construction, installation and modifications to the pilot plant have cost roughly $150,000 (Canadian) to-date. The typical monthly operating cost to maintain such a facility and conduct research of this nature in a university setting is approximately $14,000. The cost of equipment such as gas chromatographs, GC/MS, TOC analyzer, TOX analyzer, incubators and other such equipment is not included in these totals.

Place(s) of installation/application (including dates):

A pilot plant constructed with chemically inert materials (glass, stainless steel and fluorocarbons) was installed at the Rossdale Drinking Water Treatment Plant in Edmonton, Alberta, Canada in the spring and summer of 1985. The plant was modified in the fall of 1986 to accommodate the research objectives of this project.

Chemical analyses and mutagenicity testing were performed at the University of Alberta.

The draft project report was submitted in November 1987.

Patent staus, if applicable:

N/A

Other information (e.g., funding source, cooperating agencies, etc.):

The overall project cost is estimated to be $267,872. Sources of funding are as follows: American Water Works Association Research Foundation - $186,451, the University of Alberta - $62,034 and the City of Edmonton - $19,387.

In addition, Health and Welfare Canada and Supply and Services Canada provided a contract in 1984 which provided $288,295 for construction of the pilot plant.

The city of Edmonton provided the pilot plant enclosure with associated ventilation, plumbing, heating and electrical systems.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

(Publications attached)

PROJECT DESCRIPTION

Project Title:

Water Plant Optimization Study

Contact (name of person, organization, address, telephone):

K. Roberts/R. Hunsinger
Ministry of the Environment
Water Resources Branch
Drinking Water Section
1 St. Clair Avenue West
Toronto, Ontario M4V 1K6

Project Description (Please attach a schematic diagram if appropriate):

The majority of drinking water supply facilities in Ontario have treatment directed at microbiological disinfection and/or removal of suspended material.

The purpose of the Water Plant Optimization Study (WPOS) is to document and review the present conditions and determine an optimum treatment strategy for contaminant removal at the plant, with emphasis on the removal of particulate materials and disinfection processes.

The following items relate to the emphasis on particulate removal in a plant evaluation:

- Organic contaminants are often associated, at least in part, with particulates.
- Particulates themselves have health-related limits (turbidity/bacteria).
- In striving for excellence in water treatment, it is important to examine all possible approaches and requirements, but first optimum use should be made of the processes already in place.

Operator training and certification is an important component of plant optimization. Plans are already underway with the Ontario MOE/Municipal Engineers Association (MEA) to implement such a program.

The mechanism for ensuring ongoing optimization will be through an annual update by MOE staff or consultants, or a combination of the two.

The study has been organized with a team approach in mind; thus, progress reports and a meeting with the Project Committees are required as the work progresses.

It is not the intent of this study to provide a detailed implementation scheme for plant rehabilitation.

A Protocol for the WPOS was prepared which included detailed Terms of Reference and a standardized format for the Report Table of Contents (copy attached). The work tasks required the consultant to examine, in detail, three years of daily and monthly operating data, prepare a comprehensive assessment of plant operations and the level of treatment performance achieved and to provide recommendations for short and long term modifications in order to obtain optimum disinfection and contaminant removal.

Operating and cost data (including data on efficiency, results, etc.):

Forty-one water treatment plants have been studied - about 10 reports are final (end of February 1988) and all reports will be finished by April 1988.

Plant consultants chosen were generally the original designers; around 10 consultants worked on the 41 plants.

Average cost for the studies was about $35K/plant. Including internal staff time, the project has cost about $2M for the 41 plants.

Place(s) of installation/application (including dates):

Forty-one plants throughout Ontario between August 1986 to April 1988 (list attached). These plants cover around 70-75% of Ontario population on piped water.

Patent status, if applicable:

N/A

Other information (e.g., funding source, co-operating agencies, etc.):

Funded by Ontario Ministry of the Environment.

The program is to continue:

(a) to update completed studies annually; and

(b) to cover the remaining 25% population.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

MINISTRY OF THE ENVIRONMENT

Water Plant Optimization Study

Location to be Completed in February - April 1988

NO.	PLANT
1.	South Peel (Lakeview)
2.	Belleville
3.	Niagara Falls
4.	Cornwall
5.	Toronto (R.C. Harris)
6.	Port Dover
7.	St. Thomas (Elgin Area)
8.	Leamington (Union Area)
9.	Sudbury (Wanapitei)
10.	Sudbury (Ramsey Lake)
11.	Kitchener
12.	Stouffville
13.	Sarnia
14.	Sault Ste. Marie (wells)
15.	Sault Ste. Marie (St. Marys River)
16.	Brantford
17.	Burlington
18.	Grimsby
19.	North Bay
20.	Timmins
21.	Fort Erie
22.	Toronto (R.L. Clark)
23.	Hamilton
24.	Thunder Bay (Loch Lomond)
25.	Thunder Bay (Bare Point)
26.	St. Catharines
27.	Kingston
28.	Peterborough
29.	Ottawa (Britannia)
30.	Ottawa (Lemieux)
31.	Amherstburg
32.	Oshawa
33.	Wallaceburg
34.	Windsor
35.	London (Lake Huron)
36.	Toronto (Easterly)
37.	Mitchell's Bay
38.	Belle River
39.	Walpole Island
40.	Stoney Point
41.	Tilbury

CA-51

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

EMERGING WATER SUPPLY TECHNOLOGY

AWWARF Code #: CA-18

PROJECT DESCRIPTION

Project Title:

A study using computer software to model the performance of carbon adsorbers in a large Canadian Drinking Water Treatment Plant.

Contact (name of person, organization, address, telephone):

Dr. D. T. Williams, Environmental Health Centre, Health and Welfare Canada, Tunney's Pasture, Ottawa, Ontario, Canada K1A OL2.

Project Description (Please attach a schematic diagram if appropriate):

This study was designed to monitor and model the first full scale application of granular activated carbon (GAC) at a major Canadian drinking water treatment plant.

The contactors were monitored for trihalomethanes, total organic halogen and total organic carbon. Computer models, developed by Dr. John Crittenden, were used to model the adsorber performance and model predictions will be verified, where possible, with the monitoring data. The model will then be used to predict the performance of carbon contactors in other locations and to examine possible improvements to adsorber performance by changes in plant operating conditions.

Operating and cost data (including data on efficiency, results, etc.):

Predictive adsorption technology will be the major output of this work.

Place(s) of installation/application (including dates):

Start date: October 1985
Completion: March 1988

Patent status, if applicable:

N/A

Other information (e.g., funding source, cooperating agencies, etc.):

Funding: Health and Welfare Canada; Supply and Services Canada.
Study cost: $ 80K Canadian
Collaborators: Dr. P. Huck, U. of Alberta; Dr. J. Crittenden, Michigan Technological University.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

PROJECT DESCRIPTION

Project Title:

Computer modelling of adsorption of mutagens on XAD-2.

Contact (name of person, organization, address, telephone):

Dr. D. T. Williams, Environmental Health Centre,
Health and Welfare Canada, Tunney's Pasture,
Ottawa, Ontario, Canada K1A OL2.

Project Description (Please attach a schematic diagram if appropriate):

This study will determine adsorption isotherms for 2 non-volatile mutagens individually on XAD-2 resin and then predict their competitive adsorption behaviour on the resin.

Predictions will then be compared to experimental data for multi-component mixtures.

Predictive adsorption technology will be the major

Operating and cost data (including data on efficiency, results, etc.):

Predictive adsorption technology will be the major output of this work.

Place(s) of installation/application (including dates):

Location:	University of Alberta, Edmonton.
Start date:	April 1987
Completion:	March 1988

Patent status, if applicable:

N/A

Other information (e.g., funding source, cooperating agencies, etc.):

Funding:	Health and Welfare Canada; Supply and Services Canada.
Study cost:	$ 54K Canadian
Collaborators:	Dr. P. Huck, U. of Alberta; Dr. J. Crittenden, Michigan Technological University.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

FRANCE

FRANCE

PROJECT DESCRIPTION

Project Title:

Application of the combined ozone/hydrogen peroxide for the removal of organics.

Contact (name of person, organization, address, telephone):

J.P. Duguet, J. Mallevialle
Centre de Recherche de la Lyonnaise des Eaux
38, rue du Président Wilson
78230 Le Pecq (France)
(1) 39 76 64 10

Project Description (Please attach a schematic diagram if appropriate):

Chloronitrobenzenic compounds contained in stored toxic wastes have recently been identified to be the major source of groundwater pollution near wells used for drinking water production in France. Due to concern for the possible toxicity and tastes and odors problems associated with sources for the production of drinking water, an appropriate treatment for the removal of these compounds must be determined. The ozonation process is known to be an efficient treatment for the oxidation of many aromatic compounds, but in the case of the chloronitrobenzenic compounds ,the reactivity of ozone is low. The oxidation of such compounds requires a very reactive oxidant species, such as a hydroxyl radical. This can be produced by an O_3/H_2O_2 combination. The feasibility of an O_3/H_2O_2 combination for detoxifying a groundwater in France has been tested on a 450 $l.h^{-1}$ pilot plant and optimal conditions have been determined. The removal of the o-chloronitrobenzene from 1900 $\mu g/l$ to less than 20 $\mu g/l$ was achieved by applying 8 g O_3/m^3 with a 20 minute contact time. These conditions also removed a substantial amount of minor pollutants.

It is well known that due to a scavenging effect, the oxidation efficiency of the hydroxyl radical is related mainly to the bicarbonate content of the water. Depending of the wells in use, the alkalinity of the groundwater to be treated can be very large (120 to 230 mg/l as $CaCO_3$). In order to evaluate the capital and the operating costs as a function of the pollutant and bicarbonate concentration, a calculation procedure integrating the different competitive reactions of hydroxyl radical has been used and will be presented.

Operating and cost data (including data on efficiency, results, etc.):

Table IV

(see table IV in the article)

Place(s) of installation/application (including dates):

450 l/h pilot plant located in Alsace (France)

September 86 - February 1987

Patent staus, if applicable:

- French patent n° 2 563 208 April 20, 1984

Other information (e.g., funding source, cooperating agencies, etc.):

-

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

APPLICATION OF THE OZONE-HYDROGEN PEROXIDE COMBINATION FOR THE REMOVAL OF TOXIC COMPOUNDS FROM A GROUNDWATER

J.P. Duguet, C. Anselme, P. Mazounie and J. Mallevialle

Centre de Recherche Lyonnaise des Eaux-Degrémont
38 rue du Président Wilson, 78230 Le Pecq, France

P A P E R

To be presented at the

5the European Symposium on
Organic Micropollutants in the Aquatic Environment
Rome, Octobre 1987

APPLICATION OF THE OZONE-HYDROGEN PEROXIDE COMBINATION FOR THE REMOVAL OF TOXIC COMPOUNDS FROM A GROUNDWATER

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Centre de Recherche Lyonnaise des Eaux-Degrémont
38 rue du Président Wilson, 78230 Le Pecq, France

ARTICLE

To be presented at the WQTC

Baltimore, USA, November 1987

APPLICATION OF THE OZONE-HYDROGEN PEROXIDE COMBINATION FOR THE REMOVAL OF TOXIC COMPOUNDS FROM A GROUNDWATER

J.P. Duguet, C. Anselme, P. Mazounie and J. Mallevialle

Centre de Recherche Lyonnaise des Eaux-Degrémont
38 rue du Président Wilson, 78230 Le Pecq, France

SUMMARY

Nitro and chloro-benzenic compounds, which are widely used in dye industries, have been associated recently with groundwater contamination. Because of their potential toxicity and for taste and odor considerations, three main actions were decided to solve the problem. First, to follow the advance of pollution toward the wells, samples were collected automatically and analyzed using GC-MS. Results indicate that o-chloronitrobenzene was the main pollutant in concentrations ranging from 10 to 20,000 $\mu g/l$. Second, to monitor the drinking water quality, an on-line spectrophotometer was used to measure the optical density at 254 nm at the inlet and outlet of the plant. Third, the feasibility of using the O_3/H_2O_2 combination was determined at a 450 l/h pilot plant. Reduction of chloronitrobenzenes from 1.9 mg/l to less than 20 $\mu g/l$ could be reached by the application of 8 g O_3/m^3 and 3 g H_2O_2/m^3 with a 20-minute contact time. To avoid an eventual bacterial regrowth in the network due to biodegradability of the oxidation by-products, sand and GAC filtration were tested after oxidation. An evaluation of the costs of these different treatments is also presented.

1. INTRODUCTION

Organoleptic problems have always concerned the water supply industry. New techniques, such as flavor profile analysis and closed loop stripping analysis (1), provide a better understanding of taste and odor causing compounds as well as mechanisms and origins. The use of such techniques for water quality control has allowed detection of pollution caused by stored wastes. These wastes have infiltrated the soil and polluted groundwater near wells used for drinking water production.

Chloro and nitrobenzenic compounds which are the main pollutants are widely used in chemical industries for dye synthesis. These types of compounds have been associated recently with water contamination (2,3). Because of their possible toxicity (4) and their effect on taste and odor (5), the use of such water for the production of drinking water requires a sophisticated treatment in order to remove these compounds.

To solve this pollution problem, three main courses of action were undertaken. First, to follow the path of the advance of pollutants toward the wells, samples were collected from different sites by use of a continuous liquid-liquid extraction device, after which GC/MS analysis on the extract was performed in the laboratory. Second, to monitor the quality of the drinking water, an on-line spectrophotometer was used. The optical density at 254 nm (which is representative of the aromatic compounds) was measured continuously on water at the inflow and outflow of the drinking water treatment plant. Third, the feasibility of a complete treatment line comprising an O_3/H_2O_2 combination for the detoxification of the groundwater was determined. The aim of this article is to present results concerning

the optimization of such a treatment line and to give cost evaluation.

2. MATERIALS AND METHODS

Pilot Plant

The study is performed on a 450-l/h pilot. This pilot comprises : two ozone contactors (150 mm in-diameter, 4 m in height), an ozone generator (Degrémont, France) which produces up to 10 g/h, a dosage system for hydrogen peroxide which permits the injection of a diluted solution in the input of the two columns, and two filters running in parallel (sand and GAC) after the oxidation step to reduce biodegradable oxidation by-products.

Analytical Methods

Ozone concentration in the gas and dissolved ozone in water are measured respectively by the KI and indigo methods (6).

The concentration of H_2O_2 in the stock solution and the residual in water are measured using an iodometric method.

Identification and dosage of the benzene derivatives were performed using 2 types of liquid-liquid extraction. For concentrations above 10 μg/l, 1 liter of water adjusted to pH 2 was extracted by 100 ml of methylene chloride added in three times. Extract was concentrated to 1 ml using Dufton distillation columns. Two microliters were injected "on column" in a gas chromatograph (GC) (Varian 3500, USA) on a fused silica 50 m capillary column (Chrompack OV 1701). Detection and quantification were realized with a flame ionization detector. Identification was done by the use of a mass spectrometer (MS) (Finnigan ITDS, USA). For concentrations lower than 10 μg/l, a second technique was used. 1 liter of water was extracted by small volumes of benzene (2 to 5 ml). The extract was injected in GC equiped with an electron capture detector to reach sensitivity limits of 0.1 to 0.05 μg/l.

Sensory analyses used to evaluate taste and odor characteristics were threshold odor number technique (TON) and flavor profile analysis (FPA) (7,8) which gives a better description of organoleptic properties present in the sample.

The optical density at 254 nm is traced using an automatic spectrophotometer developed by the Lyonnaise des Eaux Laboratory (9).

3. RAW WATER CHARACTERISTICS

The pilot plant is fed by groundwater from a well. The main characteristics of the water are reported in Table I. The presence of low concentrations of nitrite, iron, and manganese, as well as the moderate alkalinity, are noted. The bicarbonate concentration is one of the main parameters that affect the oxidation efficiency (10).

Table II gives the evolution of pollutant concentrations in the groundwater from January to March 1987 :

- the total concentration of benzenic compounds is in the range of 1400-2500 μg/l, with an average value equal to 2100 μg/l ;
- the major pollutant (representing 70% of the pollution) is o-chloronitrobenzene (1000-1800 μg/l - average concentration : 1500 μg/l) ;
- some other pollutants, such as chlorobenzene and nitrophenol, are present in the groundwater at variable concentrations depending on the sampling period.

During this period TONs in the fed water were above 20.

4. FEASIBILITY OF DETOXIFICATION BY AN O_3/H_2O_2 COMBINATION

Introduction

Ozone has been used for many years in drinking water treatment to remove color, control tastes and odors, inactivate microorganisms, and for various other purposes. Because of its high oxidation potential, ozone is also able to oxidize organic micropollutants in water. But depending of on

their nature, oxidation kinetics can vary widely. Hoigné and Bader (10) report the reaction rate constants of ozone with different substituted benzenes, from which it can be concluded that the nitro and chloro substituents reduce ozone reactivity. Therefore, the high concentrations of chloronitrobenzenic compounds contained in the groundwater seem to be more refractory to ozone. To detoxify such a groundwater, the very reactive and oxidizing hydroxyl radical (OH°) can be used. This radical can be produced in particular by combining ozone with hydrogen peroxide (11) or with ultraviolet light (12). The first combination, which is tested in this study, has been found to be an attractive treatment for the removal of chlorinated solvents from groundwater (9). For a given raw water, the parameters which are responsible for the oxidation efficiency are the rate of radical production and the contact time. So the parameters which need to be optimized are the ozone and hydrogen peroxide dosages and the contact time. For plant design, two other parameters must be taken into account : the maximal concentration of pollutants and the alkalinity of the water. The hydroxyl radicals (OH°) are scavenged by the bicarbonate ions, therefore the oxidation efficiency depends on the pollutant concentrations/alkalinity ratio.

Results

Two types of tests are performed to verify the efficiency of ozone alone and ozone combined with hydrogen peroxide.

Ozonation

The results obtained by ozonation alone are summarized in Figures 1 and 2. The tests show that for a contact time of 30 minutes, the decrease of the optical density at 254 nm (which corresponds to the decrease of aromatic compounds concentrations) is a function of the increasing applied ozone dose. At an ozone dose of 16 g/m^3, the removal of chloronitrobenzene reaches 85%. With a constant ozone dose, the reduction of the optical density at 254 nm increases when the contact time is longer, up to 30 minutes. The application of 16 g O_3/m^3 with a 40-min contact time allows a 88% reduction of chloronitrobenzene corresponding to a residual concentration of 150 μg (o-chloronitrobenzene)/l in the ozonated water.

Oxidation by ozone alone, even for large doses of ozone and long contact times, does not allow a sufficient reduction of the chloronitrobenzene concentration, which remains higher than the desired amount of 20-30 μg/l in the ozonated water.

Combination of ozone with hydrogen peroxide

The O_3/H_2O_2 combination is performed in two columns placed in series. Operating parameters are the same in each column. Previous experiments reported in Figure 3 show that the best o-chloronitrobenzene removal is obtained for a hydrogen peroxide/ozone mass ratio of 0.4. The application of ozone and hydrogen peroxide dosages of 8 g/m^3 and 3 g/m^3, respectively, during a 20-minute contact time permitted a 99% elimination of benzenic compounds (Figure 4). An increase in the contact time to 30 minutes does not improve removal efficiency.

5. EFFICIENCY OF THE COMPLETE TREATMENT LINE

It is well-known that during the oxidation process biodegradable compounds are formed which can induce bacterial regrowth in the distribution network. To avoid this, the oxidation process must be followed by a biological treatment such as sand or GAC filtration. The latter technique has a distinct advantage in that it removes micropollutants by adsorption. For the study presented, fixed beds GAC and sand columns with 15 min hydraulic residence times are used. All of the treatment lines run for 3 months. Samples are collected weekly at different treatment steps. The mean concentrations of benzenic compounds and o-chloronitrobenzene in the water after the oxidation step are 22 and 16 μg/l respectively, corresponding to a 99% reduction. TOC removal obtained by oxidation is

about 0.3 mg/l ; this corresponds to the mineralisation of 30% of the benzenic compounds (Table III). Identification of oxidation by-products (e.g aldehydes, carboxylic acids) will follow at a later stage of the study. After GAC filtration, the treated water has a benzenic compounds concentration lower than the detection limit (1 μg/l). From raw water to oxidized water, the threshold odor number (TON) is reduced from 20 to 3, and there is no taste and odor in the GAC filtered water after 3 months of operating time. Therefore, this treatment line is very efficient and results in a high-quality drinking water. If the technical feasibility of such a treatment line can be demonstrated, investments and the operating costs of a new plant can be evaluated.

6. INVESTMENTS AND OPERATING COSTS

As previously shown the oxidation efficiency is dependent upon the organic matter concentration and alkalinity. The drinking water treatment plant uses different waters from the wells. These waters have different alkalinities and pollutant contents (120 to 230 mg $CaCO_3$/l). Therefore, it is a necessity to evaluate the increase of ozone and hydrogen peroxide dosages and resulting changements in costs for various concentrations of benzene derivatives and alkalinity. In Table IV, both investment and operating costs are calculated in the case of a 30,000 m^3/day plant, for a removal of 500 to 5000 μg/l of ortho- chloronitrobenzene (o-CNB). The investment costs for oxidation process vary from 9,5 Millions FF to 33 Millions FF, with 12 Millions FF for a 5 m/h GAC filtration, total investment cost is between 21,5 and 45 Millions FF. On the other hand, operating costs for the oxidation process and GAC filtration are varying from 0.09 to 0.49 FF. In these cases, ozone and hydrogen peroxide dosages are between 3.5 to 32 g/m^3, and 1,5 to 13 g/m^3, respectively. Table V gives an evaluation of the ozone dose as a function of the initial o-CNB concentration and alkalinity. Results show that two-fold increases in applied ozone dose are needed when the alkalinity varies from 120 to 230 mg/l as $CaCO_3$.

7. CONCLUSION

Taste and odor control can be used to detect pollution of water by industrial waste. For example, the use of the flavor profile analysis combined with the close loop stripping analysis has permitted to detect the pollution of a groundwater by chloro- and nitrobenzenic compounds in a range of 10 to 20,000 μg/l. The use of such a groundwater for the production of potable water requires a detoxification step. A promising way for the removal of such compounds is oxidation using ozone. Tests performed using ozone alone showed that even large ozone dosages do not allow to reach a satisfactory level of removal.

On the other hand the use of powerful oxidant species such as hydroxyl radicals which are formed by the combination of both ozone and hydrogen peroxide has permitted to obtain a water containing a concentration in benzene derivatives lower than 20 μg/l. This concentration corresponds to the odor threshold concentration of the main pollutant, the o-chloronitrobenzene. Furthermore this treatment reduces drastically the TON measured on oxidized water. The feasibility of such a treatment is demonstrated using ozone and hydrogen peroxide dosages of 8g/m^3 and 3 g/m^3, respectively, with a 20-minute contact time. An evaluation of the costs of such an effective treatment for the specific case studied showed, that investment and operational costs were of the same order than construction of new wells at another location and transportation of the water.

This oxidation step can be economically used to reach a satisfactory oxidation at reduced ozone dosages followed by an artificial groundwater recharge which can lead to a biological removal of pollutants and their by-products. Moreover, the oxidant dosages can be adjusted as a function of

the degree of pollution. Monitored for example by a UV spectrophotometer, this can lead to very flexible operating costs. In the case of a large decrease of the pollution to be treated, hydrogen peroxide injection can be suppressed, resulting in a classical treatment and a minimization of operating costs.

8. REFERENCES

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TABLE I. Main Characteristics of Ground Water

Resistivity (Ω/cm)	1695
pH	6.7
$KMnO_4$ oxidability (mg/l) as oxygen	1.05
TOC (mg/l)	1.9
Alkalinity (mg/l as $CaCO_3$)	225
Chloride (mg/l)	88
Sulfate (mg/l)	58
Nitrate (mg/l as NO_3)	23
Nitrite (mg/ as NO_2)	0.30
Iron (µg/l)	50
Manganese (µg/l)	30
Magnesium (mg/l)	28
Calcium (mg/l)	71

TABLE II. Evolution of Benzene Derivatives Concentration (ug/l) in Groundwater – (January-March 1987)

COMPOUNDS	1/8	1/22	1/27	2/3	2/4	2/20	3/3	3/11	3/17	3/24	3/31
Chlorobenzene	165	235	150	640	540	34	67	85	85	66	145
o-Dichlorobenzene	< 1	–	–	–	–	2	2	2	3	3	4
Benzenic compound	13	5	25	21	21	24	18	26	24	27	31
Nitrobenzene	7	9	7	5	–	10	5	7	7	3	12
Nitrophenol	280	300	17	–	–	–	96	–	98	–	187
o-Chloraniline	< 1	–	–	11	23	18	4	4	7	4	2
o-Nitrotoluene	145	152	136	120	132	120	90	165	135	125	134
m-Nitrotoluene	14	15	15	12	13	14	9	17	17	16	19
p-Nitrotoluene	20	11	12	8	–	3	8	7	10	–	14
m-Chloronitrobenzene	111	100	103	72	73	81	80	106	150	179	113
p-Chloronitrobenzene	123	–	5	–	–	–	42	–	–	–	39
o-Chloronitrobenzene	1610	1580	1560	1300	1460	1690	970	1828	1490	1320	1402
Dichloroaniline	–	–	–	–	–	6	–	–	–	–	–
Methoxynitrobenzene	7	7	6	5	5	6	3	–	5	5	8
Dichloroaniline	6	6	–	6	5	12	3	–	4	2	3
Trichloroaniline	–	–	–	–	–	–	–	–	–	–	5
Dinitrotoluene	–	–	–	–	–	–	–	–	–	–	3
TOTAL	2501	2420	2036	2200	2272	2023	1397	2247	2035	1750	2121

TABLE III. Evolution of TOC, Benzenic Compounds, o-chloronitrobenzene and Threshold Odor Number at Different Treatment Steps

RUNNING TIME (Days)	0	4	11	19	25	32	39
RAW WATER							
TOC (mg/l)	1.9	-	1.9	1.95	1.75	1.9	-
Benzenic compounds (μg/l)	2023	-	1397	2249	2031	1750	2121
o-chloronitrobenzene "	1690	-	970	1830	1490	1320	1402
TON > 20							
OXIDIZED WATER							
TOC (mg/l)	1.7	1.5	1.75	1.6	1.3	1.45	-
Benzenic compounds (μg/l)	52	6	16	21	18	19	23
o-Chloronitrobenzene "	41	4	13	14	14	14	14
TON = 3 to 5							
SAND-FILTERED WATER							
TOC (mg/l)	1.4	1.55	1.45	1.55	1.15	1	-
Benzenic compounds (μg/l)	17	6	11	35	17	11	14
o-Chloronitrobenzene "	15	3	8	28	11	8	9
TON = 2 to 3							
GAC-FILTERED WATER							
TOC (mg/l)	-	0.9	0.40	0.40	0.35	0.45	-
Benzenic compounds (μg/l)	-	< 1	< 1	< 1	< 1	< 1	< 1
o-Chloronitrobenzene "	-	< 1	< 1	< 1	< 1	< 1	< 1
TON = 1							

TABLE IV. Evaluation of the Investment and the Operating Costs as a Function of the Initial o-Chloronitrobenzene Concentration

Orthochloronitrobenzene to be removed (μg/l)	500	1000	1500	3000	5000
INVESTMENTS (30000 m^3/j)					
1) Oxidation					
Ozone g/m^3	3.5	7	10	20	32
H_2O_2 g/m^3	1.5	3	4	8	13
Contact time min	20	20	20	20	20
Cost 10^6 FF	9.5	12	15	23.5	33
2) GAC Filtration (5m/h)					
Cost 10^6 FF	12	12	12	12	12
TOTAL 10^6 FF	21.5	24	27	35.5	45
OPERATING COSTS					
Ozone FF/m^3	0.035	0.07	0.10	0.20	0.32
H_2O_2 "	0.017	0.035	0.04	0.09	0.14
GAC 2 years "	0.035	0.035	0.03	0.03	0.03
TOTAL "	0.09	0.14	0.17	0.32	0.49

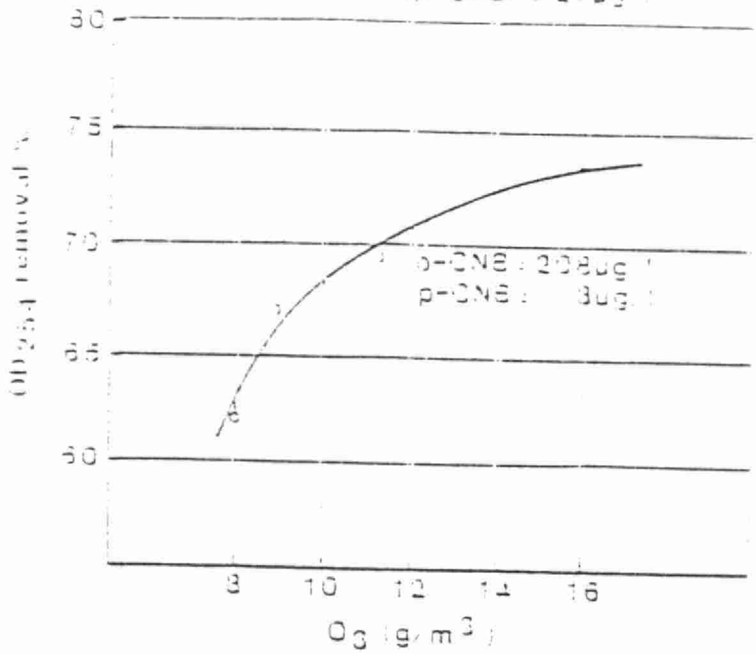
TABLE V. Evaluation of the Ozone Doses as a Function of the initial o-Chloronitrobenzene Concentration and Alkalinity

ALKALINITY mg $CaCO_3$/l	OCNB μg/l				
	500	1000	1500	3000	5000
120	2.7	5.5	8	16	27
160	3.5	7	10	20	32
250	5.5	10	15	29	43

OZONE OXIDATION

Fig.1. Influence of the ozone dosage (Contact time : 30min)

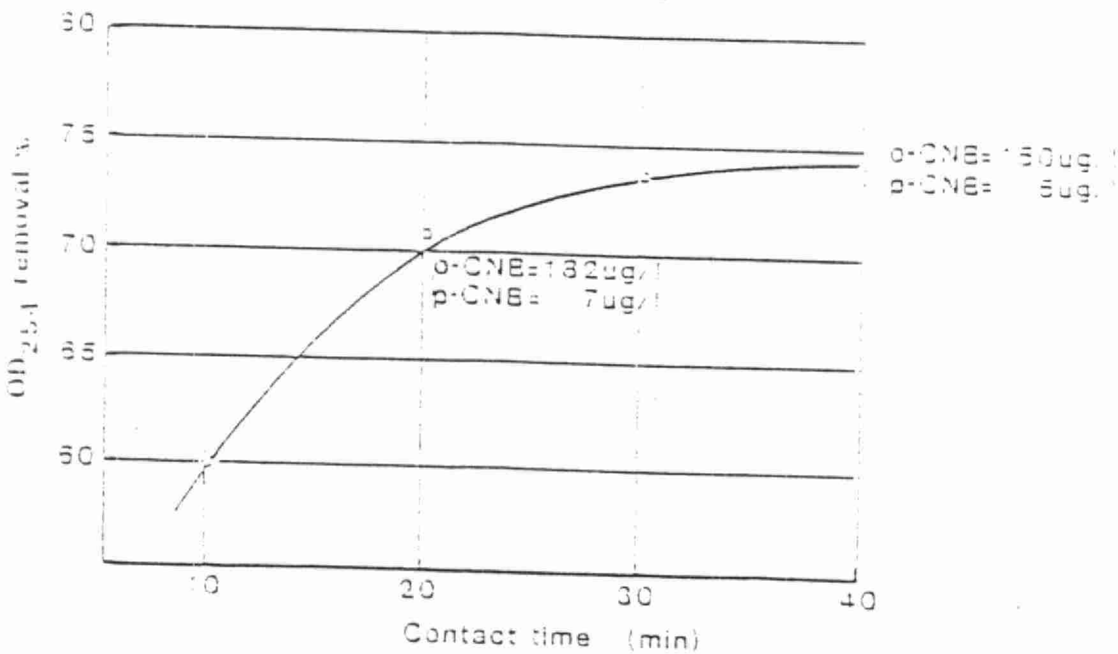
Raw water (o-CNB) = 1300μg/l
(p-CNB) = 27μg/l



OZONE OXIDATION

Fig. 2. Influence of contact time — O_3 = 16 g/m3

Raw water (o-CNB) = 1300 μg/l
(p-CNB) = 27 μg/l



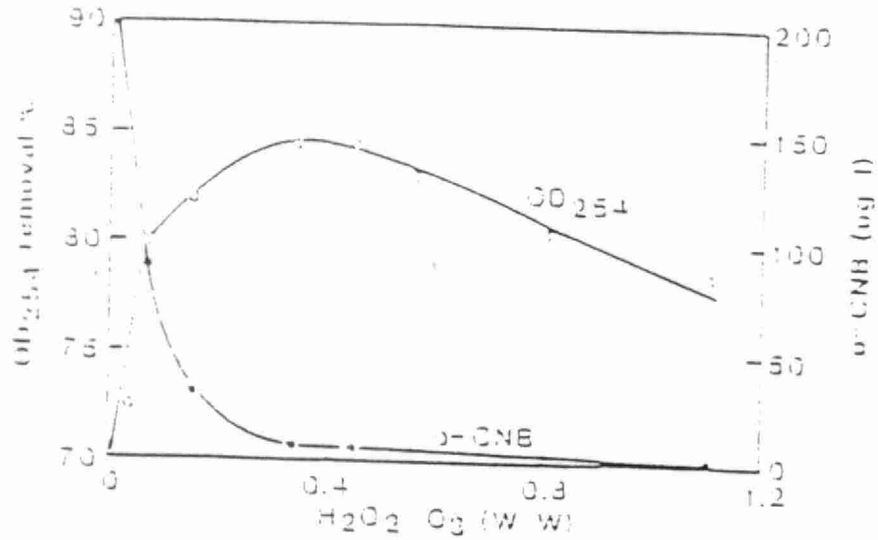


Fig.3. Influence of H_2O_2 dosage on the oxidation efficiency (ozone dosage 12g/m3 contact time 20min)

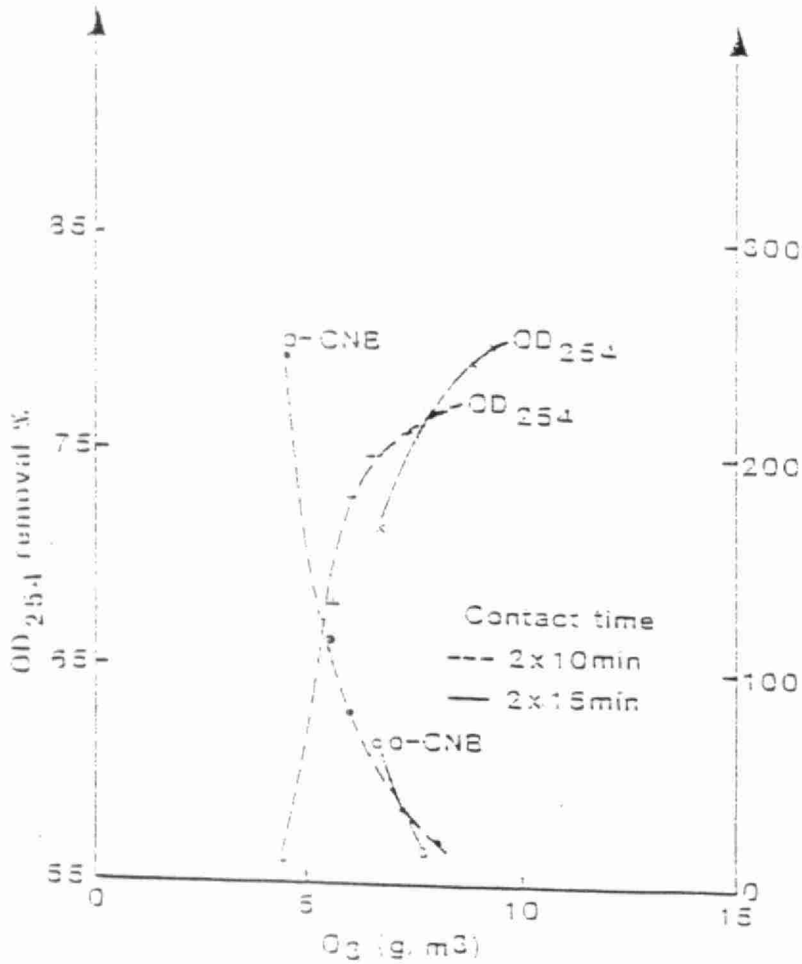


Fig.4. Removal of OD254 and o-CNB by a double O_3/H_2O_2 injection. Influence of the ozone dose and contact time (H_2O_2/O_3 : 0.4 W/W [o-CNB]$_0$ = 1800ug/l)

PROJECT DESCRIPTION

Project Title:

Improvements of the disinfection by ozone :

Influence of oxidant species

Contact (name of person, organization, address, telephone):

J.P. Duguet, J. Mallevialle
Centre de Recherche de la Lyonnaise des Eaux
38, rue du Président Wilson
78230 Le Pecq (France)
(1) 39 76 64 10

Project Description (Please attach a schematic diagram if appropriate):

Oxidants such as ozone and chlorine are largely used as disinfectants and have been the subject of many laboratory studies. The oxidation potential of ozone is more significant than that of chlorine in that its effect as a germicide is much stronger. During the last ten years, research on ozone chemistry has shown that ozone affected by OH^- ions, ultraviolet radiation, or hydrogen peroxide transforms into different radical species. The most important of these, the hydroxyl radical (OH), is much more oxidizing and reactive than molecular ozone. However, the disinfecting potential of these radicals for the treatment of water remain poorly understood.

The object of this study was to compare the relative efficiencies of molecular and radical ozone and of chlorine (as a reference) with regard to the inactivation of several types of microorganisms present in two different types of water.

In laboratory the microorganisms studied were poliomyelitis virus, the bacteria Bacillus cereus and Pseudomonas fluorescens and Scenedesmus algae. In addition, some tests were conducted on the bacteria Legionella pneumophila to define the inactivation conditions.

A series of runs was conducted on a pilot plant.

A factorial fractionnary plan of two levels was established. The parameters studied and their low and high levels were : ozone concentration in the gas phase, 2 and 5 ppm ; pH , 6 and 8 ; contact time, 3 and 6 min ; and gas-liquid ratio 10 and 20%.

Results showed that inactivation, depending on a given microorganism, at the gas liquid interface, can be related directly and principally to ozone concentration, to molecular ozone and radicals, such as OH° or others generated by pH variation, and not so much to the gas-liquid ratio and contact time. Moreover, complementary results brought on by inactivation kinetics will allow us to optimize and build mathematical models. These simulation models will permit to introduce data corresponding to waters to be treated and to predict disinfection efficiency in a given reactor.

Operating and cost data (including data on efficiency, results, etc.):

Operating and cost data not available yet.

Place(s) of installation/application (including dates):

LABORATORY PILOT, CENTRE DE RECHERCHE LYONNAISE DES EAUX

1987 - 1988

Patent staus, if applicable:

No

Other information (e.g., funding source, cooperating agencies, etc.):

-

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

PROJECT DESCRIPTION

Project Title:

New medium frequency ozone generators supplied by oxygen

Contact (name of person, organization, address, telephone):

J.M. ROVEL (Degrémont)
183, avenue du 18 juin 1940
92508 Rueil Malmaison Cedex
Tél. : 42 04 90 00

Project Description (Please attach a schematic diagram if appropriate):

Ozone generators.

To improve both yield per dielectric tube (more compact ozone reactor) and the specific energy, Degrémont/Air Liquide has introduced a new generator fed with pure oxygen but using a selective adsorbing system able to screen between O_2 and O_3, thus giving the possibility to recycle the unused O_2 to the inlet of the generator (see scheme 1).

Advantage are clear from table I which gives the main performance obtained with our medium frequency ozonator.

Operating and cost data (including data on efficiency, results, etc.):

See table I

Place(s) of installation/application (including dates):

MYRTLE-BEACH (USA)
HENRICO-COUNTY (USA)

Patent staus, if applicable:

No

Other information (e.g., funding source, cooperating agencies, etc.):

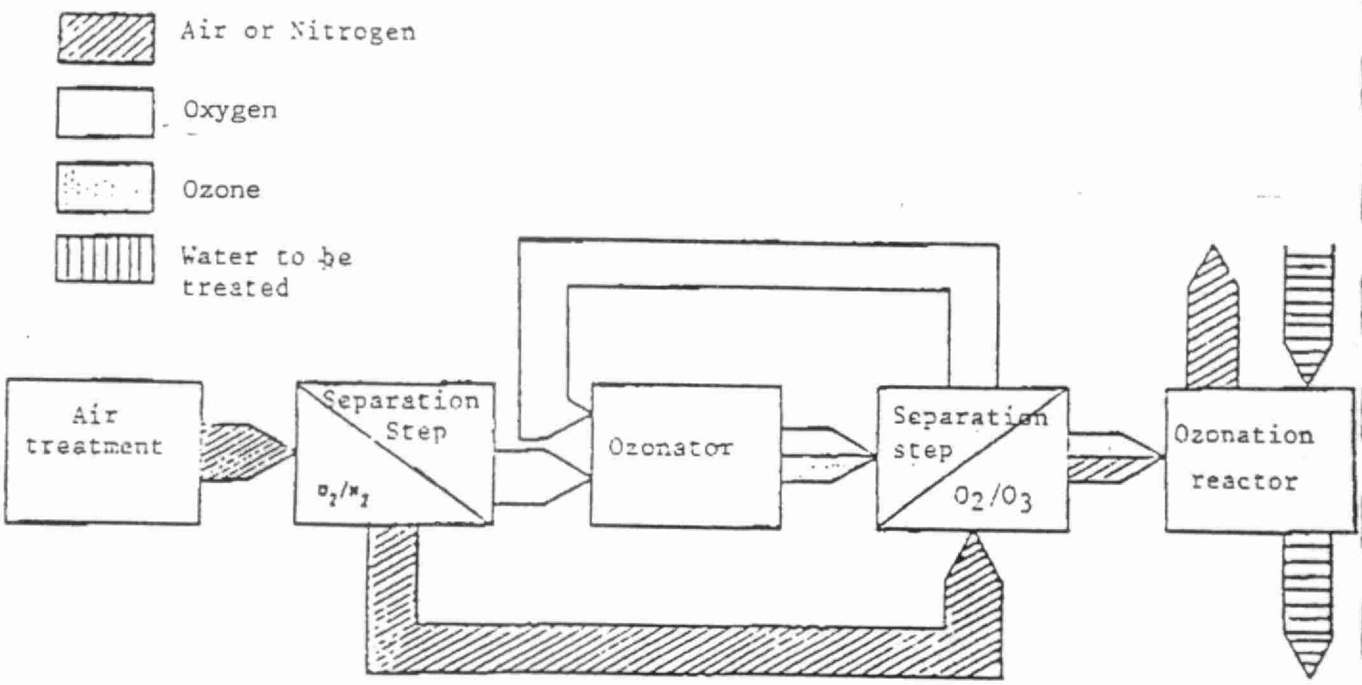
If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

TABLE I

	600 Hz Air	600 Hz Oxygen	600 Hz O_2+O_2 recycling system
U.S.A. reference	MYRTLE-BEACH (3x280 tub.)	HENRICO-COUNTY (5x202 tub.)	
Specific power ($W.\ m^{-2}$)	3260	3080	3080
Concentration ($gO_3.Nm^{-3}$)	18	70	70
Specific yield ($gO_3.h^{-1}\ m^{-2}$)	200	420	420
Total energy consumption (1) ($Wh\ (gO_3)^{-1}$)	23	20	12
Smallest unit built : tub. number	55	55	55
Production ($g.h^{-1}$)	2750	5745	5745
Largest unit tub. number	1138	1138	1138
Production ($g.h^{-1}$)	56900	119490	119490

(1) Including gas line (air or O_2 generation) - Excess O_3 destruction...

SCHEME N° 1



Air or Nitrogen
Oxygen
Ozone
Water to be treated
Air treatment
Separation Step
O_2/N_2
Ozonator
Separation step
O_2/O_3
Ozonation reactor

PROJECT DESCRIPTION

Project Title:

Combined Ozonation and Flotation. Application to the Treatment of Highly Algae-loaded Water

Contact (name of person, organization, address, telephone):

M.M. Bourbigot. Anjou Recherche. Centre de Recherche de la
Compagnie Générale des Eaux
Chemin de la Digue, B.P. 76
78600 Maisons Laffitte, France
1 - 39 62 34 56

Project Description (Please attach a schematic diagram if appropriate):

The ozone diffusion technique consist in generating very fine bubbles by sweeping porous diffusion plates with a transversal water stream.

The contacter is divided into two compartments : the first is an ozonation compartment and contains the porous plates that are swept by a current of raw water that accounts for 10% of the total influent flowrate. The downward water currents select and transport the finest bubbles through an inlet located in the bottom section of the commun wall, between the ozonation and flotation chamber. In the second compartment, flocs that are caused rise to the surface of the liquid, by bubbles adsorbed to their surface, are accumulated and concentrated in the upper quiescent zone and can be withdrawn as desired. This quiescent zone must be non-agitated and non-turbulent.

Operating and cost data (including data on efficiency, results, etc.):

The particles that are removed by flotation are the most easily floated particles such as algae.

With this process, the clogging potential of raw water is reduced by 50 to 75%. Algae are removed by 40 to 95% depending of species. The removal of organic matters, color and turbidity are improved.

Filtration cycle duration is increased by 20 to 40%.

Place(s) of installation/application (including dates):

The pilot studies have been conducted as part of development of a new potable water plant of 150.000 m^3/day and the process has been developed on a 110 m^3/h plant.

Patent staus, if applicable:

Ask for patent in the USA N°061827 of 06/10/87 (base France N°8608780 of 06/18/86)

Other information (e.g., funding source, cooperating agencies, etc.):

Financial aid was granted by A.N.V.A.R. (Agence Nationale pour la Valorisation) for the process development.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

COMBINED OZONATION AND FLOTATION

APPLICATION TO THE TREATMENT OF HIGHLY ALGAE-LOADED WATER

M.M. Bourbigot*, M. Faivre**, H. Paillard*

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ABSTRACT

The ozone diffusion technique, which consists in generating very fine bubbles by sweeping porous diffusion plates with a transversal water stream, would appear to be a promising step forward in improving ozone diffusion. It was also observed that the small size of the bubbles facilitated the flotation of clogging matter associated with algae. For the direct application of this process an enhanced flotation system was designed which combines the two processes.

RESUME

La technique de diffusion de l'ozone, qui consiste à générer des fines bulles par balayage des surfaces poreuses au moyen d'un courant d'eau transversal, constitue une étape prometteuse vers l'amélioration des processus de diffusion de l'ozone. D'autre part, il a été observé que la petite taille des bulles favorisait la flottation des matières colmatantes liées aux algues. Un système original qui combine l'ozonation et la flottation a donc été conçu pour traiter des eaux chargées en algues.

ZUSAMMENFASSUNG

Ein vielversprechendes neues Verfahren zur Steigerung des Ozoneintrags besteht daraus, daß

sehr feine Ozonblasen durch das transversale Anströmen eines porösen Diffusors erzeugt werden. Es wurde festgestellt, daß die kleinen Blasen die Flottation von algenbürtigen Substanzen, welche Filterverstopfung hervorrufen, begünstigen. Zur direkten Anwendung dieses Verfahrens wurde eine Kombination von Ozonierung und Flotation zusammengestellt.

Introduction

Ozone is used as a pretreatment to coagulation/flocculation in numerous drinking water treatment plants to improve both turbidity and dissolved organic carbon removal. Preozonation is also viewed as a means of reducing the formation of chlorination by-products. The observed coagulating effects of ozone were first employed on colored waters in the form of the miscellisation-demiscellisation process. In the past decade the flocculating effects of ozone have been harnessed in direct filtration plants and conventional flocculation/sedimentation /filtration plants. (Bablon G. et al., 1986 ; Pascal O. et al., 1984 ; Gerval R. et al., 1985 ; Chedal J., 1985; Mathonnet S. et al., 1985).

Reckhow (1985) gives a compilation of hypothetical mechanisms for the coagulating effects of ozone. At several plants, the coagulation effects of ozone have been noted to correspond quite closely to the presence of phytoplankton in the raw water. This may suggest the release or formation of polymeric flocculant. As for the polysaccharides, the flocculating effects of one particularly prominent group of algal exudates, the alginates are well known. The liberation of these surface active polymers could explain this foam occasionally formed between the months of March and October on the surface of the pre-ozone contact chambers and flocculators of certain drinking water production plants. This phenomenon is a nuisance if the facilities in question have not been designed for removing matter by scraping. The formation of floating matter highlighted two phenomena : the presence of tiny bubbles which carry the floc to the surface and a chemical reaction between ozone and algal cells (Betzer N. et al., 1979). It was therefore observed that the small size of the bubbles facilated the flotation of clogging matter associated with algae.

A process has been developed for promoting bubble formation to produce ozonation and flotation in the same tank. Flotation is a pretreatment well known in water treatment for removing floatable substances, algae or light suspended solids.

Ozone diffusion technique using fine bubbles

It turns out that the average size of bubbles produced by forcing ozonated air through porous plates can be greatly reduced when the plates are simultaneously swept by a transversal water stream (Adler P.M. et al., 1985 ; Baetz J. et al., 1986 ; Guillerd J.R., 1968). This particular injection device is obviously very attractive ; it is very simple and thus expected to work well in an industrial environment ; it is also very economical since only a small percentage of the water need to be pressurized to a relatively low pressure when compared to the other systems : a classical method that we have previously tested, consists in the saturation of pressurized water with ozonated air ; when pressure is decreased bubbles with a diameter ranged from 40 to 100 µm are obtained ; high pressures may also be obtained by very high bubble columns. The procedures are highly effective but hardly feasible because of the losses in ozone and energy.

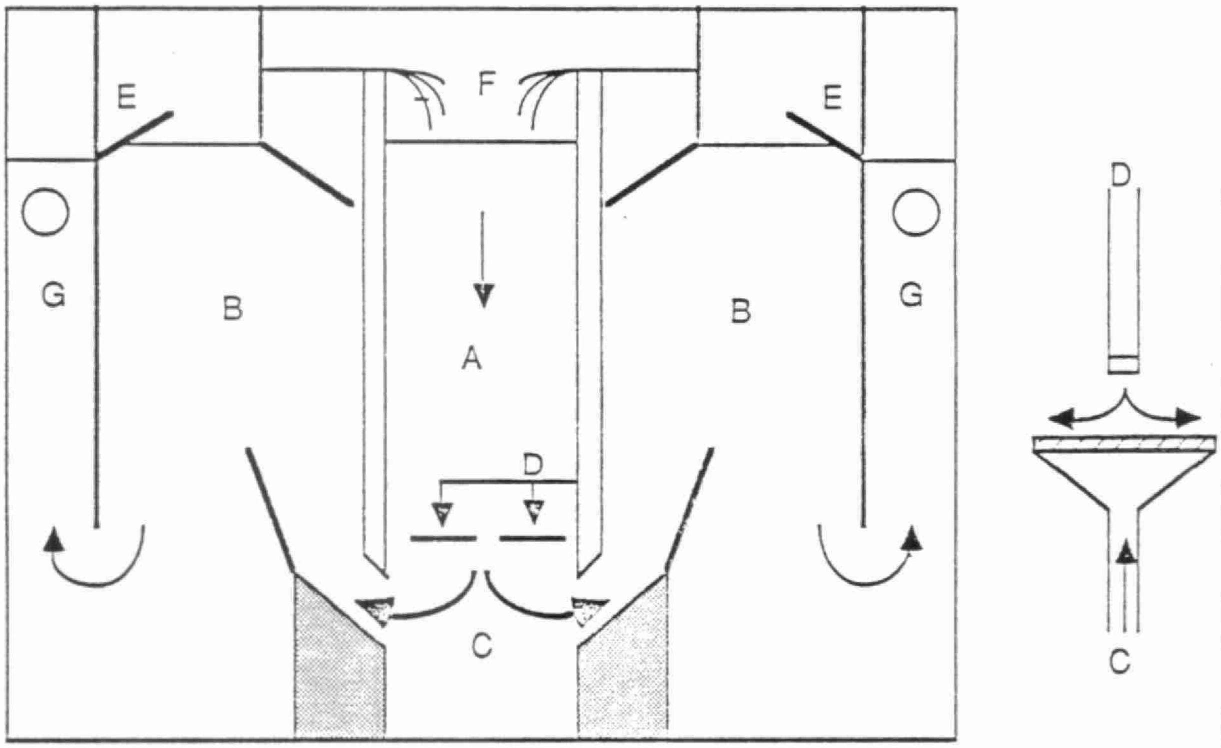
The sweeping of a porous plate by a water stream is also very beneficial in other respects. The generated bubbles are quickly dispersed in the bulk of the water column ; the turbulence caused by the water stream is likely to enhance mass transfer between the two phases. Moreover, the porous plate is continuously cleaned by the jet and potential plugging of the plate is avoided.

The first result of the substantial reduction in size of bubbles is obviously that the interfacial area between the two phases, water-gaz, would be considerably increased and the residence time of the bubbles inside the column would be much longer. So the injection device clearly have two major effects ; mass transfer is enhanced and ozone losses in the exhaust vents are reduced (Adler P.M. et al., 1985 ; Baetz J. et al., 1986).

Ozone-flotation

The contacter is divided into two compartments : the first is an ozonation compartment and contains the porous plates that are swept by a current of raw water that accounts for 10% of the total influent flowrate. The downward water currents that consist of the rest of the water to be treated, select and transport the finest bubbles through an inlet located in the bottom section of the commun wall between the ozonation and flotation chamber. The inlet is situated below the level of the gaz diffusers.

Figure 1 is a schematic representation of the ozonation-flotation structure. A patent request for this process was filed June 18, 1986 in France.



A Downflow operation chamber
B Flotation
C Porous diffusion plates
D Sweeping current (water injected through nozzle)
E Scum removal channel
F Raw water inlet
G Treated water outlet

Fig.1 : Process Development

In order to determine the optimum operating conditions for this structure we performed a number of tests on the pilot unit shown in Figure 2.

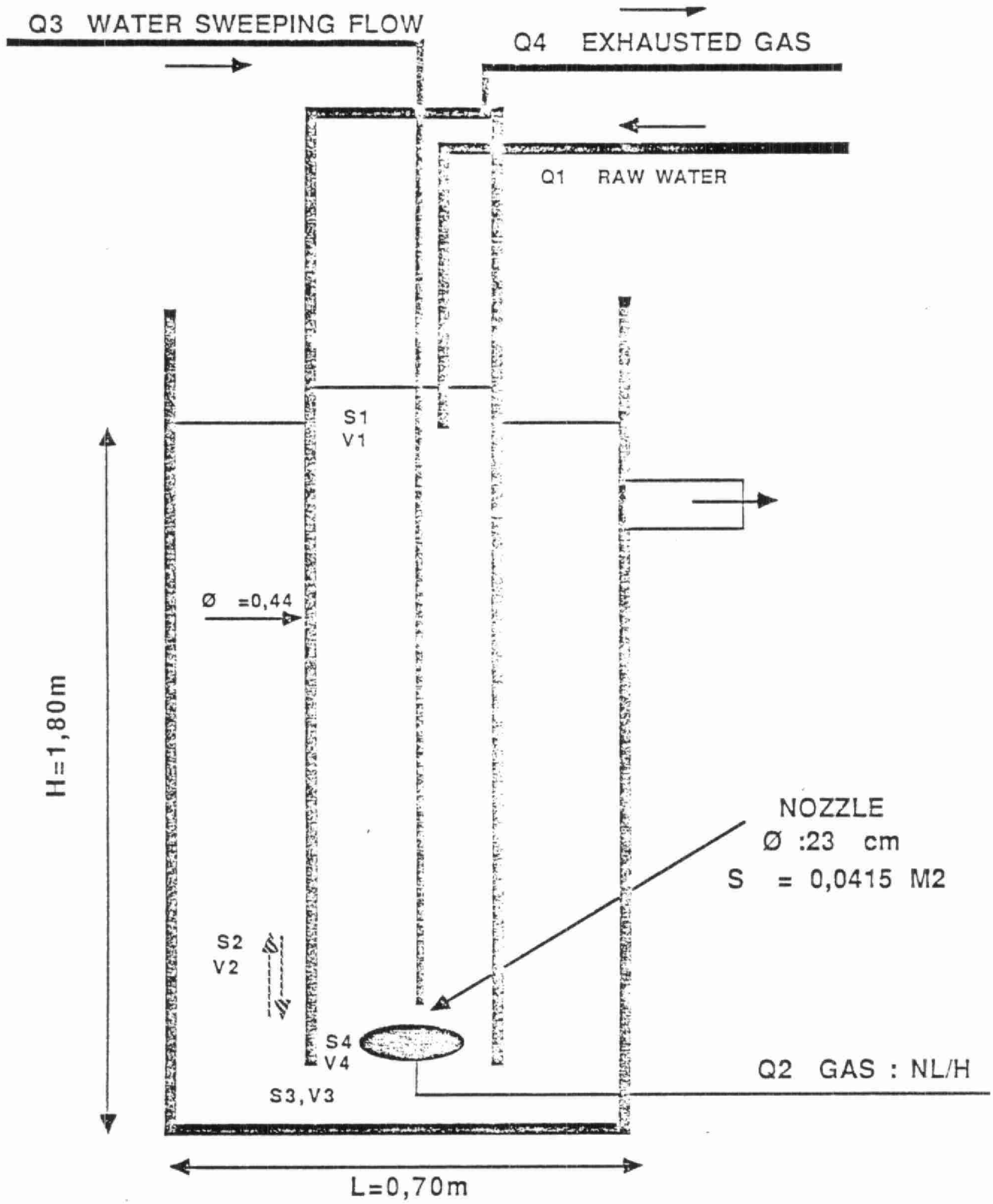


Fig. 2 : Pilot Flow Diagram

The parameters we tested were the velocity V_1 of the downflowing current in the first ozonation area, the position of the porous plate with regard to the opening between the ozonation compartment 1 and the flotation chamber 2, the velocity V_3 of passage from chamber 1 to

chamber 2 and the influence of the sweeping rate. The amount of gas dragged from chamber 1 to chamber 2 is calculated by the difference between the gas flow injected i.e. Q_2 and the gases recovered in the vents from chamber 1 i.e. Q_4.

Size of the selected bubbles

We studied the influence of the position of the porous plates and the downflow velocity of the water on the size of the gas bubbles dragged into chamber 2. Bubble size was estimated by measuring the upflowing current or by photography.

The following results were obtained (Table 1).

V_1 $m.h^{-1}$	V_a $cm.s^{-1}$	Bubble size vs. Va (diameter)	Bubble size according to photography
80	2,3 à 6,5	225 à 500 µm	214 à 550 µm
80	-	-	333 à 500 µm
80	3,9 à 4,7	375 à 400 µm	214 à 500 µm
80	1,8	200 µm	-
60	1,9 à 4,7	225 à 400 µm	250 à 500 µm
60	-	-	416 à 538 µm
60	2,6	250 µm	250 à 583 µm
40	1,9 à 2,4	225 à 150 µm	-

Table 1 : Size of bubbles selected by downflowing water velocity and dragged in second flotation chamber.

V_a = Upflowing velocity of the bubbles in the first compartment.

V_1 = Downflow current of the water in the first compartment.

The upwards velocity of bubbles according to their size is given by Wallis's formula (1969). The result of it figures in the following table :

Rb cm	va m/h
0.01	67.37
0.02	163.61
0.03	274.92
0.04	397.30
0.05	528.65
0.06	667.60

$v_a = 24\,461.60.R_b{}^{1,28}$ m/h

R_b = Radius of the bubble in cm.

During these tests, the position of the porous diffusion plates in relation to the cross-section of the passage between the two chambers varied between 100 and 50 cm.

The size of the bubbles dragged into the second chamber vary between 200 and 500 µm.

Influence of downflow velocity in ozonation chamber

Figures 3 and 4 illustrate this influence.

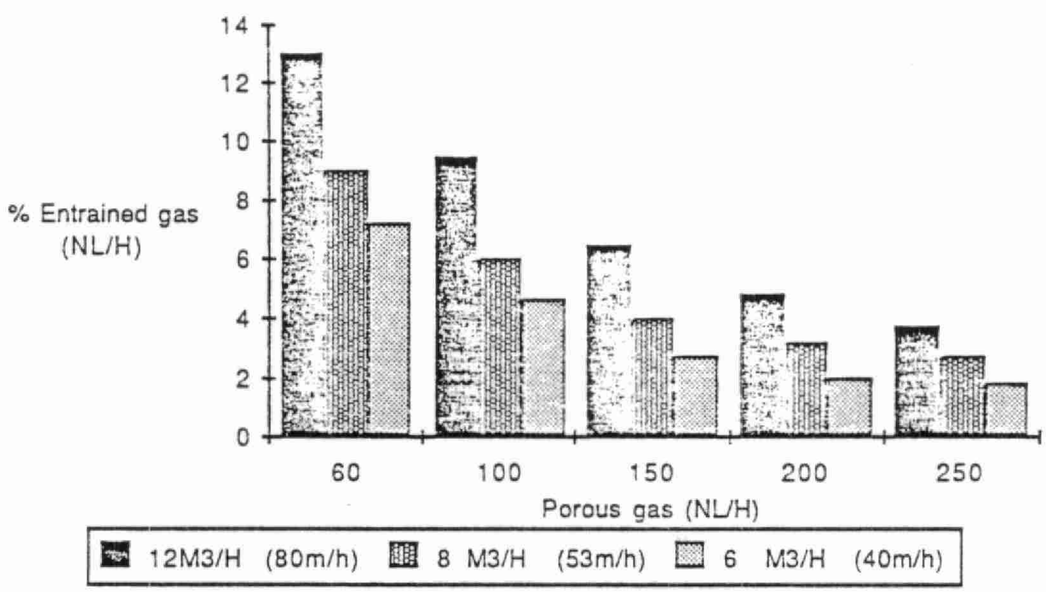


Fig. 3

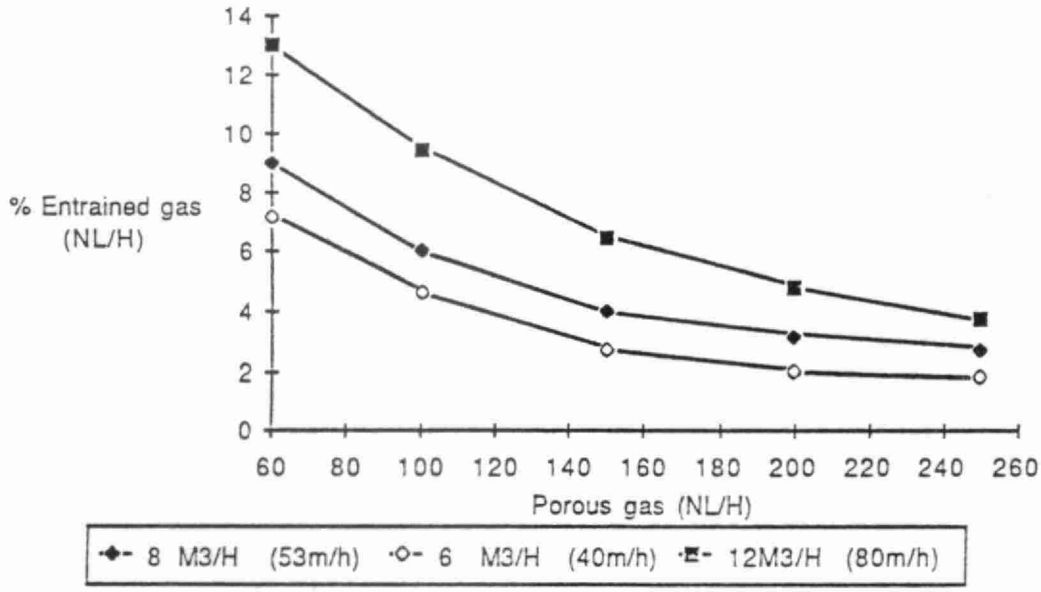


Fig. 4

Fig. 3 & Fig. 4 : Percentage of gas dragged into chamber 2 vs. the amount injected.

With a fixed gas flow rate, a certain porous plate position and a given cross-section for the opening between the two chambers, the percentage of dragged gas is proportionate to the downflow velocity.

With a fixed downflow velocity, the percentage of dragged air decreases according to the gas flow. For example, given a set downflow velocity of 80 $m.h^{-1}$ we obtain : 10% of dragged gas for 100 $Nl.h^{-1}$ of gas injected and 4% of dragged gas for 250 $Nl.h^{-1}$ of gas injected. This would seem to mean that the entrainment of fine bubbles by the water current is practically independent of the gas injection rate.

Influence of porous plate sweeping flow rate

The rate of gas dragged in the second chamber is also strongly affected by the sweeping water flow-rate applied and the jet pressure.

If we vary the pressure between 0.7 b and 2.5 b and the sweeping flow rate between 5% and 10% of the total constant water flow, the amount of dragged gas can be multiplied by 2.5 (Figure 5).

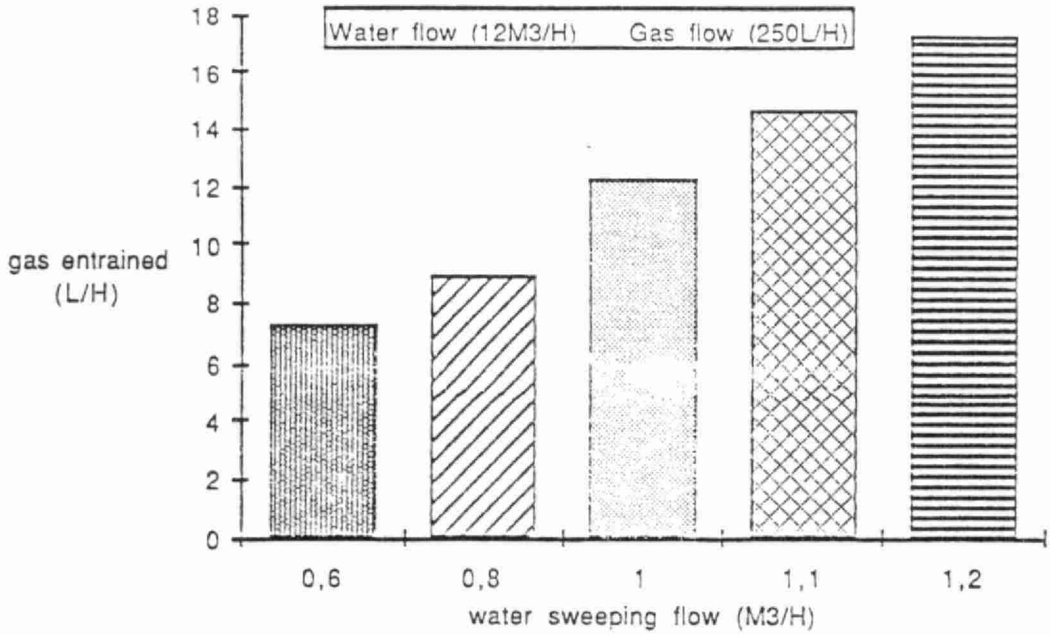


Fig. 5 : Amount of dragged gas in fonction of waterstream flow.

The larger bubbles are not selected by the water current because their velocity is too high. They rise into the upstream part of the ozonation compartment. As bubbles rise, the ozone is transferred to the water. It is important to separate the ozonation and flotation chambers because of the turbulence that would result from the large bubble size, which could disturb the formation of the floated sludge.

Flotation zone

In the second compartment, flocs that are caused to rise to the surface of the liquid by bubbles adsorbed to their surface are accumulated and concentrated in the upper quiescent zone, and can be withdrawn therefrom as desired. This quiescent zone must be non-agitated and non-turbulent.

The particles that are removed by flotation are the most easily floated particles such as algae ; the denser particles stay suspended in the water that is transferred to the filters. The water outlet is located in the bottom of the chamber. The velocity of water in this compartment must be maintained at around 20 $m.h^{-1}$ in order to avoid carrying the bubbles along.

Conclusion

The reactor can be designed to be installed upstream of a direct filtration step and downstream of a rapid blending stage where a coagulant is injected.

With this process, the clogging potential of raw water is reduced by 50 to 75%. With water that is slightly turbid, colored and high in algae content, by injecting the coagulant up-line from the ozonation-flotation tank, a top quality filtered water (turbidity of 0.1 NTU) can be obtained using ozone dose of between 0.4 to 0.8 g/m^3. Filtration cycle duration is increased by 20 to 40% and a slight saving on the amount of flocculant used was also noted. These pilot studies have been conducted as part of the development of a new potable water plant of 150 000 m^3/day and the process is now developed on a 110 m^3/h plant.

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PROJECT DESCRIPTION

Project Title:

Aerated Nitrifying Filters : Extending the Limits of Biological Ammonia Removal

Contact (name of person, organization, address, telephone):

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Project Description (Please attach a schematic diagram if appropriate):

Biological nitrification can limit chlorine demand and eliminate taste problems.

Cold water temperatures and high nitrogen concentrations can become limiting. The biological nitrification at low temperatures and varying ammonia content (up to 4 mg/l N-NH_4) are evaluated on pilot filters.

Different media heights and filtration velocities are tried to find the optimum hydraulic conditions. The concentrations of ammonia are varied to relate removal efficiency with detention time and volumetric loading. The response of biological filters to seasonally changing raw water characteristics was verified.

Operating and cost data (including data on efficiency, results, etc.):

The seeding process with groundwater at 12°C took 4 weeks for *Nitrosomonas* installation. The reactors were then able to eliminate 1 mg/l of ammonia at a filtration velocity of 10 m/h.

When returning to the original water concentration of 0.2 mg/l N-NH_4, the filter height was reduced and velocities increased to maintain the same volumetric load as applied kg N-NH_4 per m^3 media volume and day. Complete nitrification could be obtained at void volume residence time of less than 3 minutes.

If sufficient oxygen is provided by air injection, eliminated nitrogen loads can be multiplied as compared to spray oxygen dissolution. This was confirmed in a simulation of a rapid surge in nitrogen concentration as occuring with increased runoff at heavy rainfall. Nitrogen elimination is then limited by initial seeding capacity but not by filtration velocity or dissolved oxygen content. Studies are under way to assess the limiting temperature and pH values.

Place(s) of installation/application (including dates):

The pilot filters are operated on site at two different locations in line with existing treatment facilities. On site A slight ammonia and phenol pollution of the aquifer generated taste problems after desinfection with chlorine. Site B is a surface water treatment plant where the concentration of ammonia and organic material as well as the river temperature fluctuates widely during the year. The chemical oxydation of ammonia and organic material by break point chlorination forms undesirable by-products and taste.

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

PROJECT DESCRIPTION

Project Title:

Study of biofilm build-up in potable water distribution systems

Contact (name of person, organization, address, telephone):

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J.Chéron, NANCIE, 149, rue Gabriel Péri, 54500 Vandoeuvre-lès-Nancy, FRANCE
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Project Description (Please attach a schematic diagram if appropriate):

- Study on the design and engineering of an experimental pilot network, including a study on the similarity between the design as defined and a real network, distributing potable water, both as regards the hydraulic aspect and physical, chemical and biological phenomena - Building the experimental pilot facility.

- Development of a method of monitoring the experimental network, especially with regard to the characteristics of the nutrients present in the water. The object is to identify and quantify biomass in suspension and fixed on surfaces, as well as to measure the activity of such biomass and the quality of the water being transported.

- Work on the modeling of a pilot network incorporating the growth and activity of biofilm as well as its relationship with the quality of the flowing water.
Attempt ot extend modeling to the behaviour of a real-life network.

- Modeling of disinfectants fixed biomass inter-reactions.

Operating and cost data (including data on efficiency, results, etc.):

Place(s) of installation/application (including dates):

Pilot installed at International Water Center, Nancy, France, since 1986

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

Collaboration between Compagnie Générale des Eaux, Ile-de-France water board, the Seine-Normandy Basin Authority, Pont à Mousson LTd, and Nancy Urban Community.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

BIOFILM GROWTH IN DRINKING WATER NETWORK :
A PRELIMINARY INDUSTRIAL PILOT PLANT EXPERIMENT

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ABSTRACT

Bacterial population (measured as total, actively respiring and plate count) were analysed during drinking water transport within an industrial network pilot plant comprised of six loops serially disposed. PVC and cement coupons were exposed to the water flow using especial sampling devices. In the absence of any residual chlorine, bacterial growth was rapid (doubling time 10 h) during the first 40 hours. Beyond that period plateau a stationary and even a decline phase may be observed. Fixed biomass is around 10^7 bacteria per square centimeter and decreased constantly with the distance from the feed point of the network. Substrat conversion really control biofilm formation.

KEYWORDS

Drinking water, biofilm, water distribution, network, growth and decay rate, PVC, cement.

INTRODUCTION

Numerous microorganisms may be found in drinking water as bacteria, fungi, yeasts, ... (Hinzelin and Block, 1985 ; Maul et al., 1985 ; Olson and Nagy, 1984). Their presence may be the cause of water quality degradation during the distribution as they interact with coliforms isolation (LeChevallier and McFeters, 1985), amplify secondary corrosion, generate bad taste and odors, may help to the survival of macroinvertebrates *Asellus* (Levy et al., 1986). Also the control of such microbial populations and particulary the heterotrophic plate count is a key point for a better distribution.

High heterotrophic count in drinking water may be explained by several parameters which are :

(1) introduction of bacteria into the system and survival characteristic of that microorganisms under chlorine residual (Ridgway and Olson, 1982).

(2) hydraulicity and residential time,
(3) biofilm formation (Bryers, 1987),
(4) growth of bacteria using assimilable organic carbon (Van der Kooij and Hijnen, 1982 ; Joret and Levi, 1986, Pascal et al., 1986),
(5) density of particles in the water column,
(6) temperature (Fransolet et al., 1985),
(7) characteristics of the material of the pipe (Schoenen, 1986)... and so on.

Now the question is not only to recognize the importance of these parameters but to discriminate them in order to classify their rank of importance or their interaction. Only such a strategy may really help in the understanding of the so called aftergrowth phenomena for example, but also in management decision (at the level of the water treatment plant) as in monitoring.

Then, this experimental study has been designed to investigate both biofilm formation on different material coupons (PVC, cement), its interaction with bacteria evolution and with other quality parameters such as chlorine residual in drinking water network pilot plant. The pilot plant used has been builted on purpose to control most of the parameters as water flow (around 1 m/s) residential time (from few hours to several days), temperature, water quality influent and to prevent any external contaminations.
That study gives preliminary results which show the evolution of the water characteristics along the distribution system (between 0 and 10 days of retention time) and the biofilm accumulation and persistence on different materials.

Material and methods

Pilot plant

The industrial pilot plant used in that study is comprised of six loops serially disposed (Figure 1). For each loop (31 meters in length, 100 mm in diameter, cement lined cast iron) the water flow velocity was around 1 m/s and the theoritical residence time of 40 hours/loop (240 hours or 10 days for the all pilot). The table 1 gives most of the parameters characterizing the pilot plant.

TABLE 1 Hydraulic Parameters Of The Experimental Network

Water flow velocity	1 m/s
Water flow rate	n l./h
Residence time loop	40 h
Total residence time	240 h
Reynolds number	10
Velocity gradient	438/s
Peclet number	10
Rugosity coefficient	1 mm
(lambda)λ	0.0385
Laminar flow	full turbulence
Viscosity	0.01 Stokes

From previous study of simulation not reported here, we may assume that each loop works like a perfectly mixed reactor when the all pilot plant is equivalent to an infinit tubular reactor with high axial dispersion coefficient.

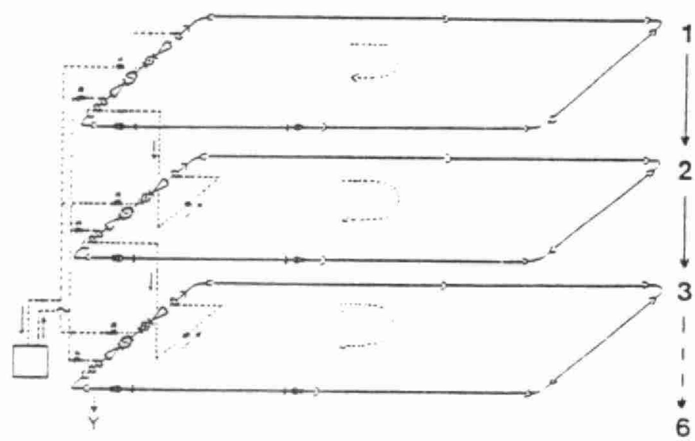

Fig. 1. Schematic representation of the drinking water network pilot plant

During the experiment, the pilot was fed with finished drinking water from the surface water treatment of the city of Nancy (Imbeaux water treatment plant). The source of

supply is the Moselle river coagulated with alum. After rapid sand filtration and ozonation, GAC filtration, lime and chlorine are added to the finished water. Breakpoint chlorination is used to carry free chlorine through the treatment process steps. The average parameters (chemical and microbiological) measured on water collected at the intake of the network plant during the experimental period August - October 1987 are given in the table 2.

TABLE 2 Selected Chemical And Microbiological Parameters (means) Measured On Finished Water At The Intake Of The Pilot

Parameter	Average value
Temperature (°C)	25*
pH	5.8*
Total chlorine (mg/l)	0.6
Free chlorine (mg/l)	0.4
Heterotrophic plate count (C.F.U./ml)	4×10^2
Active bacteria (cell/ml)	2.4×10^3
Epifluorescence count (cell/ml)	2.6×10^5
Particles (/ml)	
1-5 µm class	1,419
6-10 µm class	70
11-40 µm class	19
NO_3^- (mg/l)	5.11
Org.N (mg/l)	0.1
TOC (mg/l)	2.0
AOC (mg/l)	0.09
$P-PO_4$ (mg/l)	0.06

* inside the pilot plant

Analytical methods

Attached bacteria were removed from the surface of PVC or cement coupon by 2 min ultrasonication in 25 ml of pH 7 tris buffer solution (bacteria free). The total number of bacteria was counted by microscopic observation under UV light after filtration on black polycarbonate Nucleopore membrane (0.22 µm porosity) of the stained bacteria with acridine orange (0.02 % A.O. final concentration, 30 min. contact time).
The actively respiring bacteria (active bacteria) were counted with a microscope according to the modified technique of Bitton and Koopmann (1982). Briefly the bacterial suspensions are incubated for 2 h at room temperature with yeast extract, nalidixic acid and iodo-nitrophenyl tetrazolium or INT (0.3 g/l, 0.02 g/l and 0.2 g/l final concentration respectively). The samples + 1 ml of malachite green solution (0.1 % final concentration) are filtered through polycarbonate Nuclepore membrane (0.22 µm porosity) and the actively respiring bacteria (with red spots of formazan inside the cells) are counted. The bacteria able to grow on agar medium are quantified by classical method using agar medium without glucose (AFNOR NFT 90-402) and expressed as number of colony forming units (CFU) after 15 days of incubation at 22°C ± 1°C.
All the bacteriological results were expressed as bacteria per square centimeter of material tested or per milliliter when water samples were analysed.
Chemical analyses performed on water samples included pH (Quick 99314 pH meter), nitrogen forms, phosphates, carbon... Nitrates after reduction into nitrites and nitrites were analysed by reaction with sulfanilamide and the N naphtylethylene which give a colored complex susceptible to spectrophotometric measurement at 537 nm (Afnor NFT 90013 method). Organic nitrogen was measured after conversion into nitrates by alkaline potassium persulfate treatment at 21°C for 45 min. (LeCloirec et al., 1983).
Total organic carbon (T.O.C.) was determined using a Dohrmann T.O.C. analyser and the manufacturer's instructions. Assimilable organic carbon (A.O.C.) was measured using the slightly modified technic proposed by Van der Kooij and Hijnen (1982). The maximal number of *Pseudomonas fluorescens* P17 obtained after 3 to 6 days of incubation at 25°C was converted into mg of acetate C equivalent/liter.

Design of the study

PVC and cement circular coupons (2.0 and 2.3 cm^2 water exposed surfaces respectively) were puted inside the water pipes of each loop using especial sampling devices which allow to located the exposed surface of the tested coupons at the level of the internal pipe wall and then to submit the coupon surfaces to the true hydraulic conditions occuring inside the network. PVC and cement coupons were layed on the pipes at Day 0 when the all pilot plant was working from several weeks and was considered at steady state. Then the coupons were sampled three weeks after the Day 0 when biofilm formation was considered, according to our unpublished previous studies, at steady state.
The coupons were sampled aseptically and submitted to the analyses whithin the next two hours. The water samples were proceeded in the same way.
Because the chlorine residual (combined and free) was consumed within the first loop (40 h residence time) it can be assumed that the all system was chlorine free.
Analytical results obtained from water samples are presented in the paper as a function of the time from 0 to 240 hours according to the fact that the water flows from one loop to another one and then that it is acceptable to link the experimental points. However for biofilm analysis, data are plotted according to the number of each loop (number 1 to 6) where the coupons are sampled.

Results

Bacteria in the water column

The number of bacteria at the intake of the experimental network is relatively high as shown in the table 2 and they are enough time (at minima 40 h for the loop), enough biodegradable organic matter (90 µg/l of A.O.C. in average) and good temperature (25°C) to support bacterial growth. Data presented on the figure 2 express clearly such a bacterial bloom especially within the first loop.
The apparent growth rates calculated from the bacterial counts at the intake and the outtake of the loop N° 1 (40 hours hydraulic retention time) show that apparent µ are 2 to 10 folds higher within the first 40 hours comparatively to the other sections of the network (up to 40 hours) (Table 3). When comparing the three types of bacterial numeration, the plate count agar (C.F.U.) gives the most efficient signal of bacterial growth. The ratio epifluorescence active bacteria/C.F.U. changes between the intake and the outtake from 100/0.9/0.13 to 100/4.2/1.1.

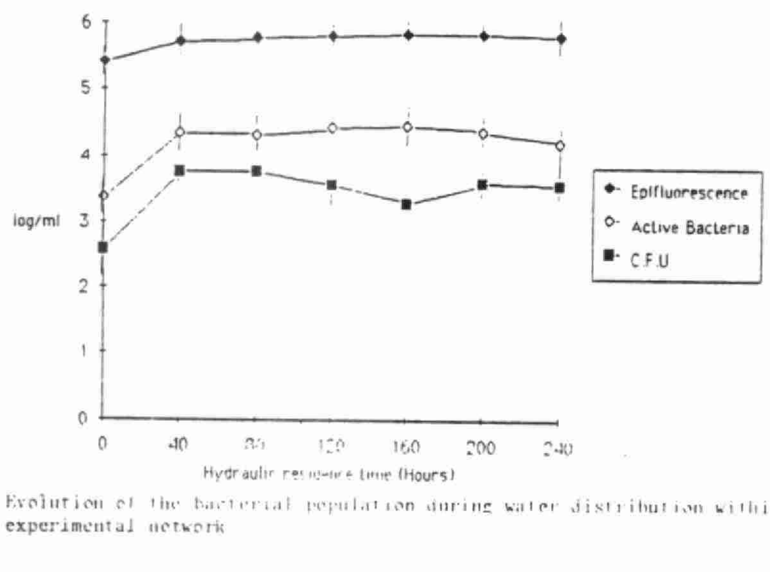

Fig. 2. Evolution of the bacterial population during water distribution within the experimental network

However, beyond the first 40 hours the apparent growth rate is very low and a decline phase may be observed quiet rapidly with heterotrophic plate count (after the second loop - 80 hours hydraulic retention time) then with active bateria (after 100 hours) and then with epifluorescence (beyond 200 hours). The apparent decay rates (Kd, hour-1) are equal to 0.010, 0.004 and 0.003 respectively and show that heterotrophic plate

counts which increase the most rapidly decrease the first and the most rapidly too (Table 3). Now when considering the last section of the network (160 to 240 hydraulic retention time) something like cryptic growth (Mason et al., 1986) may be noticed with the heterotrophic plate count that complicates definitively the picture of the system.

TABLE 3 Parameters Characterizing Growth And Decay Of The Bacterial Population Within The Distribution Pilot Plant

Type of numeration	Apparent growth rate (μ : h^{-1}) and apparent doubling time (g : h)		Decay rate (Kd) (h^{-1})
	during the first 40 hours	beyond 40 hours	
Epifluorescence count	0.018 (g = 38)	0.0017 (g = 407)	0.0003
Active bacteria	0.056 (g = 12)	0.0019 (g = 364)	0.004
Heterotrophic plate count (C.F.U.)	0.065 (g = 10)	0.003 (g = 231)	0.016

Nutrients in the water column

Heterotrophic bacterial growth is supported only by nutrients (organic carbon, nitrogen, phosphates) found in the water directly or indirectly (through the metabolism of the biofilm itself). Then it is not surprising that those parameters change during water transport within the network.

Organic carbon expressed as T.O.C. (Figure 3) decreased significatively within the first loop from 2.04 to 1.41 mg/l and consequently shows a very nice negative correlation with bacterial growth. In parallel, surprisingly, A.O.C. expressed in relatively arbitrary units (acetate C equivalent) represents only 5 % of the T.O.C. and decreases only of 20 µg/l. Beyond the second loop (up to 50 h hydraulic retention time) T.O.C. concentrations increase constantly as some bacterial molecule releases occur in our system.

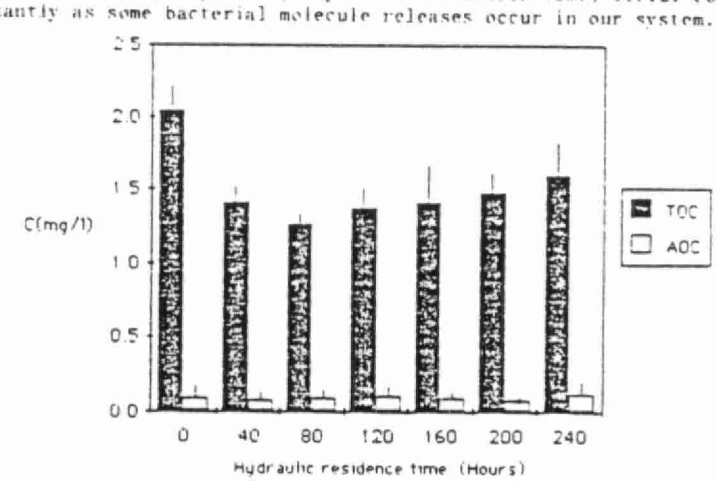

Fig. 3. Organic carbon (T.O.C. and A.O.C.) evolution during water distribution within the experimental network

Organic nitrogen even at low concentration disappears during water transport in 80 hours and then some releases occur after 120 h hydraulic retention time (Figure 4). Beyond 160 hours (loop N° 4) uncomplete denitrification process starts with intermediary nitrite formation.

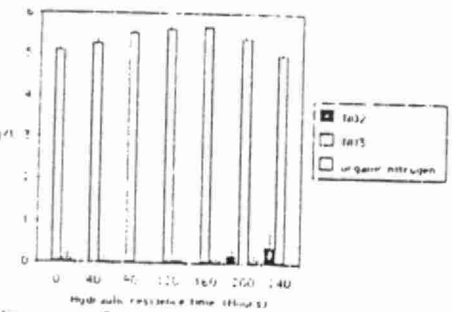

Fig. 4. Nitrogen forms evolution during water distribution within the experimental network

Biofilm formation

As pointed out by Bryers and Characklis (1982) and Bryers (1987), biofilm formation is the result of several processes, bacterial density in the water and transport, adhesion, growth, shear related removal... In the pilot used in that study : water velocity, temperature, total bacterial density are quiet equivalent in all points of the network. However, figure 5 shows clearly an evolution from loop to loop of the fixed bacteria density.

If considering the cement coupons in the loop number 1, the total bacterial population is equal to 1.0 x 10^7 per cm^2 which is quiet equivalent to several published observations (Donlan and Pipes, 1988 ; Olson and Nagy, 1984). The ratio epifluorescence count active bacteria/heterotrophic plate count in loop 1 is equal to 100/16.2/5.5. It is definitively different of the ratio calculated in the flowing water (100/4.2/1.1) and changes drastically between loop 1 and n (100/3.4/0.7).

In truth, such an observation expresses the fact that fixed biomass decreases from the intake to the outtake of the pilot at different "kinetic" according to the parameters measured.

When calculating the linear regression between the number of the loop and the log of fixed biomass per cm^2 (Table 4), the slopes of the curves are systematically negative showing that biofilm formation is limited even if the bacterial density is quiet constant in the water.

TABLE 4 Characteristics Of The Linear Regression Between The Number Of The Loop (x) And The Number Of Fixed Bacteria Per Square Centimeter (y)

Type of numeration	PVC coupon		Cement coupon	
	slope	Y origin	slope	Y origin
Epifluorescence count	- 0.033°	6.75	- 0.066*	7.4
Active bacteria	- 0.10**	6.12	- 0.19*	6.47
Heterotrophic plate count (C.F.U.)	- 0.25**	5.95	- 0.21*	5.98

* correlation coefficient significative at 0.01 % level
** correlation coefficient significative at 0.05 % level
° correlation coefficient no significative

Whatever the nature of the material studied (PVC or cement) higher is the distance from the intake of the network, lower is the fixed biomass density. That decrease in biomass density is very sensitive whith heterotrophic plate count (around 95 %) comparatively to epifluorescence count (around 45 %). Again this difference in the behavior of total bacteria and living bacteria could be related to the nutrient limitation in water and by way of consequence to the biofilm specific growth rate decrease.

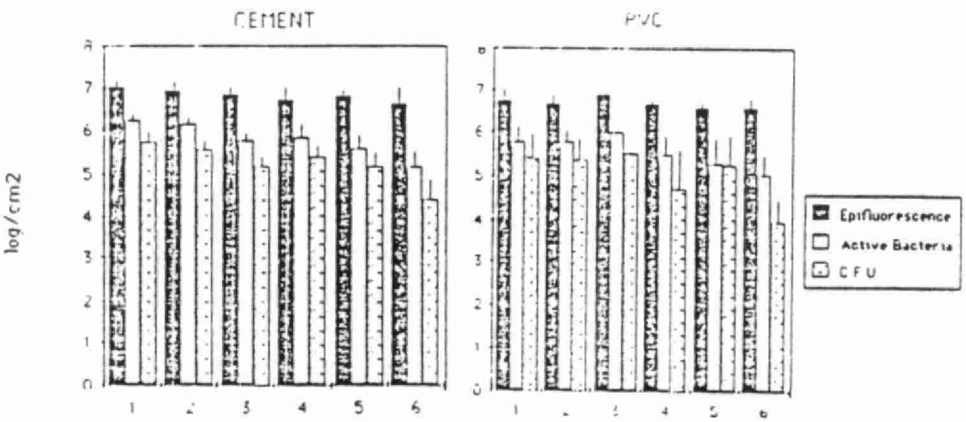

Fig. 5. Fixed bacterial density

ACKNOWLEDGMENTS

This work was done by the STELOR research group with the technical and financial support of Nancie, District urbain of Nancy, Pont à Mousson S.A., Anjou Recherche, Syndicat des Eaux d'Ile de France and Agence Financière de Bassin Seine Normandie.

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PROJECT DESCRIPTION

Project Title: Implementation of a test protocol for polyethylene pipes used in drinking water distribution systems

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Project Description (Please attach a schematic diagram if appropriate):

INTRODUCTION

Consumer complaints related to water supply are generally concerned with either taste and odor or metering problems. The sensitivity of consumers to taste and odor characteristics of distributed water has forced producers to devote more attention to this problem ; perhaps in excess of that dictated by health considerations. The nature of compounds responsible for these problems is, with few exceptions, not well known. Moreover, in the last few years, the use of synthetic pipes (eg. polyethylene) for drinking water distribution, has been rapidly increasing. However in some cases, changes in drinking water organoleptic properties have been noticed concurently with the use of HDPE pipes. Three principle causes for these changes have been identified in the literature :

- dissolution of the polymer additives,
- oxidation of the internal surface of the pipe and dissolution of the resulting polar compounds,
- migration of external contaminants through the pipe.

This study focuses on the role that high density polyethylene (HDPE) pipes may play in the degradation of drinking water quality in the distribution system. In addition, a test protocol has been implemented to select HDPE pipes suitable for drinking water distribution systems.

Both laboratory and field conditions were reported and demonstrate unambiguously the appearance of numerous organic compounds associated with an intense taste and odor problem during the passage of drinking waters through various polyethylene pipes. Batch experiments showed that two principal mechanisms are involved in the occurence of organoleptic changes caused by defective polyethylene tubings :

- dissolution of the polymer additives, and particularly alkyl phenols derived from the well-known antioxidant BHT, at concentrations exceeding 1 ug/l ;
- oxidation of the internal surface of the pipe during extrusion with subsequent release of the resulting polar compounds (aldehydes, ketones).

Twenty per cent of the 264 pipes tested appeared to be defective and the total release time may exceed a year under low flowrate conditions. Figure 1 indicates that the initial peak of TOC observed disappears after the passage of 4 m^3 corresponding to a ratio of rinsing-volume to volume of the pipe equal to 1000. On the other hand the release of total phenolic additives is more gradual and 20 % of the initial release is still observed between a rinsing ratio of 7,500 to 100,000. The concentration of total phenolic additives is constant and equal to approximately 2 μg/l between rinsing volumes of 20 and 400 m^3. The threshold taste number remains very high ($\geqslant$ 10 units) up to a rinsing volume of 100 cubic meters.

Place(s) of installation/application (including dates):

. Different locations in France.

. Development of a polyethylene pipe with characteristics adapted to drinking water distribution systems, without impairment of water quality (chemical and organoleptics properties).

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

INFLUENCE OF POLYETHYLENE PIPES ON

TASTES AND ODORS OF SUPPLIED WATER

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SUMMARY

A case study is reported that demonstrates the appearance of numerous organic compounds associated with an intense taste and odor problem during the passage of a drinking water through a 300 m polyethylene pipe. Batch experiments showed that two principal mechanisms are involved in the occurrence of organoleptic changes caused by defective polyethylene tubings, dissolution of the polymer additives (e.g., alkylphenols) and oxidation of the internal surface of the pipes during extrusion with subsequent release of the resulting polar compounds (aldehydes, ketones, etc). Of the 264 pipes tested, 25% appeared to be defective, and the total release time may exceed several months under low flow rate conditions.

Over the last few years, the use of synthetic pipes (e.g., polyethylene) for drinking water distribution has been rapidly increasing (13). In addition to corrosion considerations, their extensive use, in the case of high-density polyethylene (HDPE), is motivated by favorable mechanical properties, ease of handling during manufacture, and low permeability to external contaminants (5). However, in some cases, changes in the organoleptic properties of drinking water have been noticed concurrently with the use of HDPE pipes. Three principal causes for these changes have been identified in the literature :

- Dissolution of the polymer additives (7).

- Oxidation of the internal surface of the pipe and dissolution of the resulting polar compounds (8).

- Migration of external contaminants through the pipe (12).

This paper reports a case study that clearly demonstrates the appearance of numerous organic compounds during the passage of drinking water through a 300-m polyethyelene pipe in relation to an intense taste and odor problem, and focuses on the role that HDPE pipes may play in the degradation of drinking water quality in distribution systems.

MATERIALS AND METHODS

Laboratory and field conditions were tested. Laboratory samples were obtained by passing tap water through various sections of an HDPE conduit with respective internal diameters of 26, 34, and 40 mm. The water velocity was 3 m/min. Field samples were taken from HDPE

portions of distribution systems located in a southern suburb of Paris. Organoleptic qualities of the various samples were evaluated using Flavor Profile Analysis (FPA) and the Threshold Taste Number (TTN) according to Standards specified for the European Community (1). The FPA technique was developed for the food industry (3) and has been recently extended to analyze of tastes and odors in water samples (10). Erlenmeyer flasks and a temperature of 45°C were adopted for odor evaluations. A panel of four or more trained "tasters" evaluated the organoleptic qualities, giving a description and an intensity for each taste, odor, and sensation observed, with regard to a list of approximatly 25 descriptors. The scale for intensity was 0 (absent), 1 (threshold), and 12 (strong), with five intermediate values.

Chemical analyses initially involved closed loop stripping analysis (CLSA) and was later supplemented by steam distillation extraction (SDE). The CLSA technique used for broad spectrum analysis was similar to that used by Grob (9). The water bath and carbon trap temperatures were maintained at 45°C and 55°C, respectively. The methodology described by Nickerson and Likens (14) was followed in applying the SDE as a complement to the data obtained by CLSA. The SDE technique involves a batch extraction of 3 liters of water. Water and solvent (50 ml of methylene chloride) are heated separately, after which they are condensed together. The condensate separates into two phases, and the solvent is recovered for subsequent concentration (approximately 250 µl), using a set of small Dufton distillation columns. By the nature of the technique, SDE is expected to collect compounds of higher molecular weight and higher polarity than does CLSA. Moreover, this analysis is particularly adapted to sensory measurements by the GC/"sniffing" technique.

The resulting extracts were analyzed both by GC/FID (Carbo Erba Fractovap 4160, Italy) and GC/MS (Ribermag R10-10C, Rueil Malmaison, France). In these two cases, analytic methodology was as follows :

- On-column injection of 1 µl on a capillary chromatographic column (Chrompack OV1701 50 m long or J and W Scientific DB5 30 m long)

- Electronic impact at 70 eV

- Mass range 20-400.

RESULTS

Case Study

In the south of Paris during the summer of 1984, the connection of three HDPE sections to a cast steel pipe (Fig. 1) resulted one month later in numerous complaints of intense plastic tastes. The low water velocities in this part of the distribution system probably favored the appearance of this phenomenon. Four water samples were collected (see Figure 1) from each section of the HDPE and the cast steel pipe for sensory evaluation and specific organics analysis.

Sensory evalutation (table 1) showed that the plastic odor appeared along section 1 and occurred at a maximum intensity in section 2.

The CLSA chromatograms obtained for each sampling point (Fig. 2) indicate the appearance of numerous organic contaminants during the passage of drinking water along the HDPE pipe, with highest peak

intensities detected in sections 2 and 3. As seen in Table 2, the main products identified by GC/MS correspond to polymer additives (6, 15) (lubricants, antioxidants, stabilizing agents) and polar compounds (aldehydes). The quinone detected may be derived from BHT, the well-known phenolic antioxidant (4-methyl-2,6-di-T-butylphenol) reacted with residual chlorine present in the pipe (0.2 ppm). Some of these additives were found at concentrations exceeding 1 µg/l, progressively increasing from section 1 to section 3. Aldehydes are also found at unusually high concentrations in the last two sections.

To better understand the additives, a HDPE sample of section 2 was obtained and cut into thin slices, of which 10 g was placed in 1 liter of mineral water (Evian, France) and allowed to soak for 48 hours. Subsequent closed-loop stripping and GC/MS analysis of the soak water (Fig. 3, Table 3) allowed the identification of a broader range of additives : in addition to the compounds previously mentionned, several plasticizers were found and the presence of BHT was confirmed. This product may be directly used as an antioxidant or may be derived from the commonly used thio-bis-phenols.

Quality Control of Various HDPE Samples

Since the role of HDPE in the degradation of organoleptic properties was clearly evidenced, it seemed necessary to control the quality of the pipes available on the French market. A total of 264 HDPE samples was tested according to the following procedure : 2-m sections were rinsed with tap water (flow rate : 700 l/h) during 1 hour and then were sealed with brass caps and left in contact with tap water over a period of 12 hours. The threshold taste numbers (TTN) determined for these samples are reported in Table 4. It can be seen that 20% of the pipes tested presented a TTN exceeding the limit fixed by the European Community (threshold 3 at 25°C). Among the defective pipes, more than 50% showed TTN values higher than 30.

Complementary parameters were measured for three typical samples (high, medium and low taste intensity determined by FPA) and are summarized in Table 5. Nonspecific parameters such as UV absorbance or CH_2 index are significantly increased ; the taste intensity does not seem to be directly related to the concentrations of the released additives. Because the total yields of polar compounds (aldehydes and ketones) increase with increased taste intensity, it can be assumed that these polar compounds play a role in establishing the final organoleptic sensation.

Raw HDPE Granules

To determine the relative influences of the polymer itself and manufacturing process (pipe extrusion), raw granules of polyethylene with Thio-bis-phenol as an antioxidant additive, were left in contact with mineral water (Evian, 100 g/l, 48 h), which was then analyzed by CLSA-GC/MS. Compared with the extract of section 2 soak water, similar concentrations of the same additives were found, but there was a complete absence of the polar compounds. The ratio (S) of contact surface to water volume that we applied in the raw HDPE granules study is equal to that of HDPE pipes with internal diameters of 30 to 50 mm (S=1 to 1.5 cm^{-1} for a PE specific surface of 20 cm^2/g). Therefore, we can assume that these compounds are formed by oxidation of the internal surface of the pipe during the cooling phase following the extrusion, in the presence of air (4, 7, 8, 11).

Sensory Evaluation of the Additives

A GC-sniffing method was used in an attempt to identify the specific additives involved in the odor problem. In this procedure, the effluent of the capillary chromatographic column is split into two parts, 30% supplied to the FID detector and 70% to the operator nose. Figure 4 represents the GC-odor chromatogram of a sample of section 2 soak water, extracted by methylene chloride with a steam-distillation-extraction technique. The basic burnt plastic odor detected in the waters studied was found to be caused by component number 4, BHT. Two other aromatic compounds also revealed a plastic odor. However, it must be kept in mind that other molecules found below their odor threshold in the SDE extract may also have been involved in the final odor detected by the consumers : e.g., 2,2,4-trimethylpentan-1,3-diol-di-isobutyrate (plasticizer), the odorous property of that was checked with a pure standard. Furthermore, since the compounds are smelled separately, the method does not account for the synergistic effects that are probably occuring in such a complex mixture, in particular the polar oxidation by-products.

Evolution of Desorption Products in a Polyethylene Pipe

In the case study reported above, the taste and odor problem casted four months (even after long periods of rinsing) finally leading to the replacement of the pipe.

To obtain information on the duration of the release, a polyethylene pipe (32-mm internal diameter) was flushed with a given volume of water (rinsing volume) and then sealed. After a 48-h soaking period, with a ratio polymer contact area/soak water volume fixed at 1 cm^{-1}, TOC, phenols concentration, UV absorbance at 260 nm, and TTN value were determined in the soak water. Figure 5 indicates that the initial peak of TOC observed disappears after the passage of 4 m^3, corresponding to a ratio rinsing volume/volume of the pipe equal to 1000. On the other hand, the release of total additives is more gradual and 20% of the initial release is still observed between a rinsing ratio of 7,500 to 100.000. The concentration of total phenolic additives is constant and equal to approximately 2 µg/l between rinsing volumes of 20 and 400 m^3. TTN remains very high at about more than 10 units up to a rinsing volume of 100 cubic meters. Moreover, UV absorbance at 260 nm is higher in soak water than in rinsing water. All of these investigations indicate that the release duration can exceed one year under low flow-rate conditions, with defective polyethylene pipe (e.g., polyethylene pipes with thio-bis-phenol as an additive).

Influence of the Nature of the Antioxidant and of the Extrusion Conditions on the Organoleptic Properties of HDPE Granules

As a consequence of all these field and batch experiment results, we can assume that the use of an antioxidant with lower solubility than thio-bis-phenol or 4-methyl-2,6-di-ter-butyl-phenol (BHT) is probably a way to solve taste and odor problems occurring with HDPE polymer. Despite this fact, another important parameter seems to be the extrusion conditions apply during the manufacture. The results shown here are part of a study presently under investigation, to find an improved formulation for HDPE pipes. Two different antioxidants were chosen, one with effective solubility in water (BHT) and the other with theoreticaly no solubility in water (Irganox 1010, see structure of this compound in Figure 6). Granules of HDPE polymer were prepared

with these two compounds, alone or in combination, at a mass temperature of 200°C and with an air or nitrogen purge during the extrusion operation.

Extractions of these different granules were then realized under the following conditions :
- ambiant temperature
- mineral water
- 24 hours of soaking
- 100 g/l of PE pellets (S = 1.25).

The resulting soaked waters were then extracted by SDE in order to determine the concentrations of BHT and degradation by-products of antioxidant additives, and by batch liquid/liquid extraction for the determination of Irganox 1010 release. Analyses were then performed by GC/MS for SDE extracts and by HPLC with UV detection at 280 nm (16,17) for Irganox 1010 quantification. In addition, TTN values were determined for every water sample. All the results are shown in Table 6.

From these results, it seems to be clear that the higher the BHT concentration, the higher the TTN increase. However, this phenomenon is much more evident under air extrusion conditions, probably because of an enhancement by traces of polar-released compounds that remain undetected or unidentified in this experiment.

TTN values measured on the granules extraction are not higher than those detected with HDPE pipes, perhaps for two main reasons :

- use of another antioxidant than thio-bis-phenol
- lower formation of polar compounds during extrusion.

In this experiment, Irganox 1010 is the better antioxidant because the TTN's obtained are lower than the European Community specification (TTN < 3). While Irganox 1010 is submitted to a high degradation (see Figure 6) under air extrusion conditions, BHT may play a protective role for this additive, as indicated by the comparison between the last two columns of the Table 6. Finally, despite the fact that very high concentrations of phenolic additives (10 to 100 µg/l) and degradative by-products of these additives (2.5 to 3 µg/l) are detected on HDPE pellet-soaked waters, it seems certain that extrusion with nitrogen purge has a positive action on the organoleptic properties, and that the less soluble the additive, the more easily the taste and odor problems are resolved.

CONCLUSIONS

The case study reported in this paper is a typical example of the degradations occurring in drinking-water distribution systems. Passage through a defective HDPE pipe leads to a nonpotable water with regard to the standard specifications of the European Community. Besides exceeding values of TTN, this water presents concentrations of phenols that approach the maximum allowed (10 µg/l) ; these remain undetected by the standard aminoantipyrine method (2). With these high values and the possible transformation (phenols/quinones) of some desorbed compounds, more toxicological information is required. The problem sources and their possible remedies are summarized in Table 7.

If the water velocities in the distribution system are difficult to control, the use of an antioxidant with lower solubility than thio-bis-phenols (Fig. 7) seems to be the most appropriate solution. However, since all of the antioxidant additives seem to be composed of two or more phenolic rings, it can be assumed that the decomposition of these compounds should lead to an important level of phenols after the passage of drinking water in HDPE pipes. It should be noted that the US Food and Drug Administration (FDA) prohibited the antioxidant 4,4-thio-bis(3-methyl-6-tertiobutylphenol) (7,8). Oxidation during extrusion could be prevented by the use of an inert atmosphere (nitrogen) and the use of lower temperature during extrusion (200°C as a maximum). Unfortunately, the latter solution appears to be too expensive. Thus an agreement between French water distributors and HDPE pipe suppliers now provides for organoleptic quality control of each set of manufactured tubings, ensured by the extrudeurs themselves.

ACKNOWLEDGMENTS

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TABLE 1. Flavor Profile Analysis

	CAST STEEL PIPE	HDPE PIPE		
		SECTION 1	SECTION 2	SECTION 3
TASTE AND ODOR	-	BURNT 4 PLASTIC	BURNT 12 PLASTIC	BURNT 8 PLASTIC
THRESHOLD TASTE NUMBER	1	5	50	30

TABLE 2. Additive Concentrations in HDPE Pipe

ADDITIVES	CONCENTRATION NG/L			
		HDPE PIPE		
	CAST STEEL PIPE	SECTION 1	SECTION 2	SECTION 3
LUBRICANT				
ALKYL NAPHTALENE	—	—	350	900
ANTIOXIDANTS/STABILIZING AGENTS				
4 ETHYL-2.6-DI-T-BUTYL PHENOL	—	—	70	120
ALKYL THIOPHENE	—	90	500	1800
4 METHYL-2.6-DI-T-BUTYL QUINONE	—	500	2000	3300
ALDEHYDES	50	80	500	600

TABLE 3.. *Additive Concentrations in HDPE Maceration*

ADDITIVES	CONCENTRATION NG/l
LUBRICANT	
ALKYL NAPHTALENE	4300
ANTIOXIDANT	
4-METHYL-2.6-DIT-BUTYL PHENOL	2600
4 ETHYL-2.6-DIT-BUTYL PHENOL	70
1,5-DI-T-BUTYL-3.7-DIMETHYL BICYCLO HEXANE-2-ONE	350
ALKYL THIOPHENE	1600
PLASTICIZERS	
2,2,4-TRIMETHYL PENTANE	250
1,3-DIOL DI ISOBUTYRATE	
TRIBUTYL PHOSPHATE	160
PHTALATES	660

TABLE 4.. *Threshold Taste Number (TTN) of 264 HDPE Samples*

- FLOW RATE : 700 l/h
- RINSING TIME = 12 HOURS
- CONTACT TIME = 12 HOURS

TTN	NUMBER OF HDPE SAMPLES		% OF TOTAL	
0	212		80	
3-10	13		5.0	
10-20	2		0.8	
20-30	6	52	2.3	20
30-40	11		4.2	
50	20		7.6	
TOTAL	264		100	

TABLE 5. Comparatives analyses of Various HDPE Pipes

PIPES	A	B	C
Plastic Taste Intensity	2	8	12
CH_2 index ug/l	80	80	300
UV 200 nm	0.16	0.19	0.405
UV 270 nm	0.091	0.171	0.194
Aldehydes ng/l	480	570	1400
Ketones ng/l	220	500	1100
Alkyl phenols ng/l	1000	3000	500
Alkyl napthalen ng/l	530	3150	250
Alkyl quinone ng/l	120	520	100

TABLE 6. Phenolic Additives Released from HDPE Granules

ANTIOXIDANT	IRGAN.	BHT	IRGAN. + BHT	IRGAN.	IRGAN. + BHT
EXTRUSION	N2	N2	N2	AIR	AIR
TTN	< 3	> 5	> 3	3	> 5
BHT ng/l	150	94.000	44.000	350	29.000
IRGANOX 1010 ng/l	37.500		7000	11.000	21.000
4 ETHYL-2,6-DI-T-BUTYL PHÉNOL ng/l	-	-	-	950	600
4 PROPYL-2,6-DI-T-BUTYL PHENOL ng/l	-	-	-	650	100
X COMPOUND ng/l	1100	-	1000	2900	1000
2,6-DI-T-BUTYL QUINONE ng/l	-	-	-	250	100
4 METHYL-2-T-BUTYL PHENOL ng/l	-	-	-	300	-

Table 7. Organoleptic Quality Problem Source and Remedy

ORGANOLEPTIC QUALITY PROBLEM SOURCE	REMEDY
- LOW WATER VELOCITIES IN THE DISTRIBUTION SYSTEM	--
- RELEASE OF HDPE ADDITIVES	- USE OF ANTIOXIDANT WITH LOWER SOLUBILITY THAN THIO-BIS-PHENOL → NEW FORMULATION
- SURFACE OXIDATION OF HDPE PIPES	- EXTRUSION UNDER NITROGEN ATMOSPHERE - LOWER TEMPERATURES

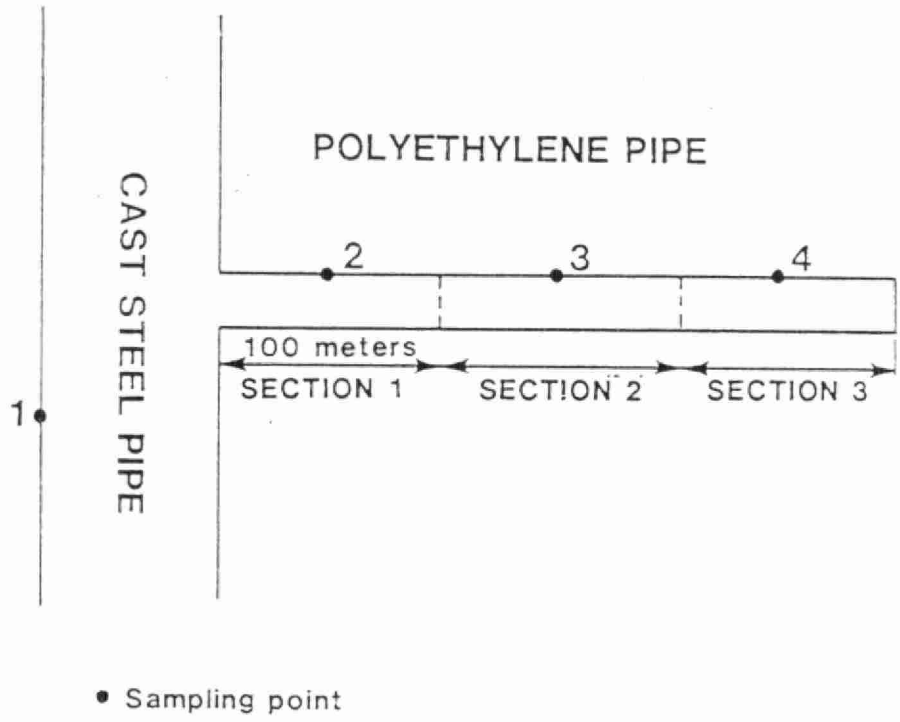

Figure 1. Case Study

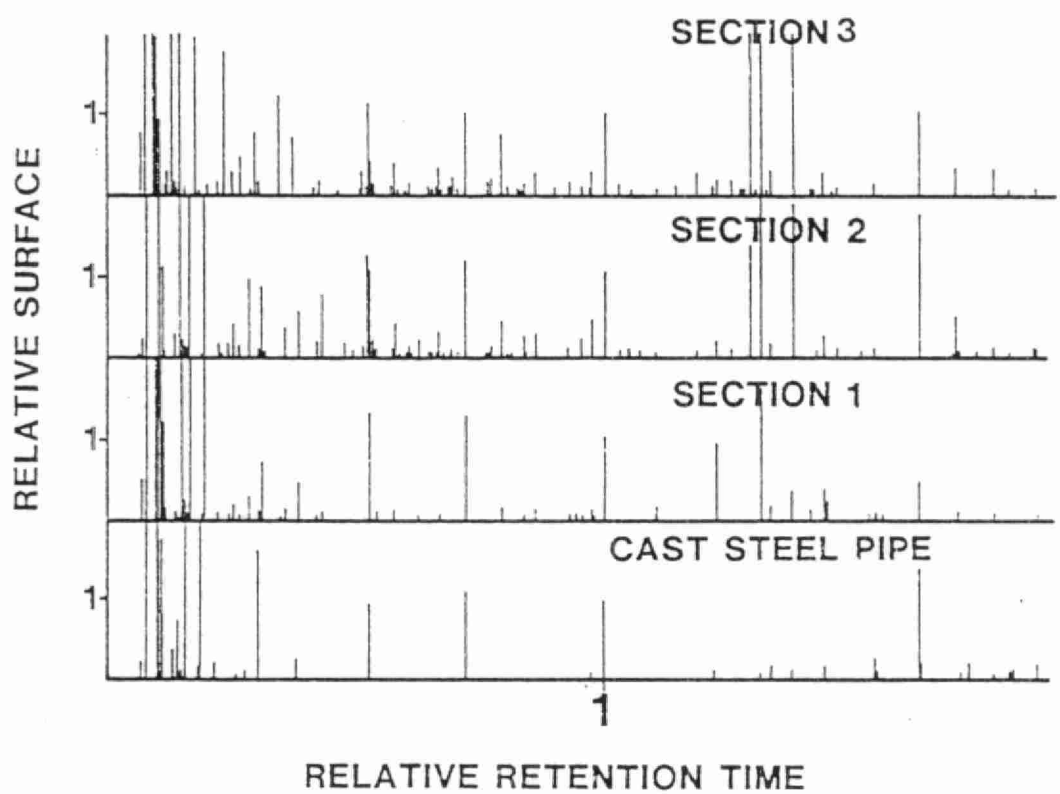

Figure 2. Analysis of Water Samples CLSA/GC/FID

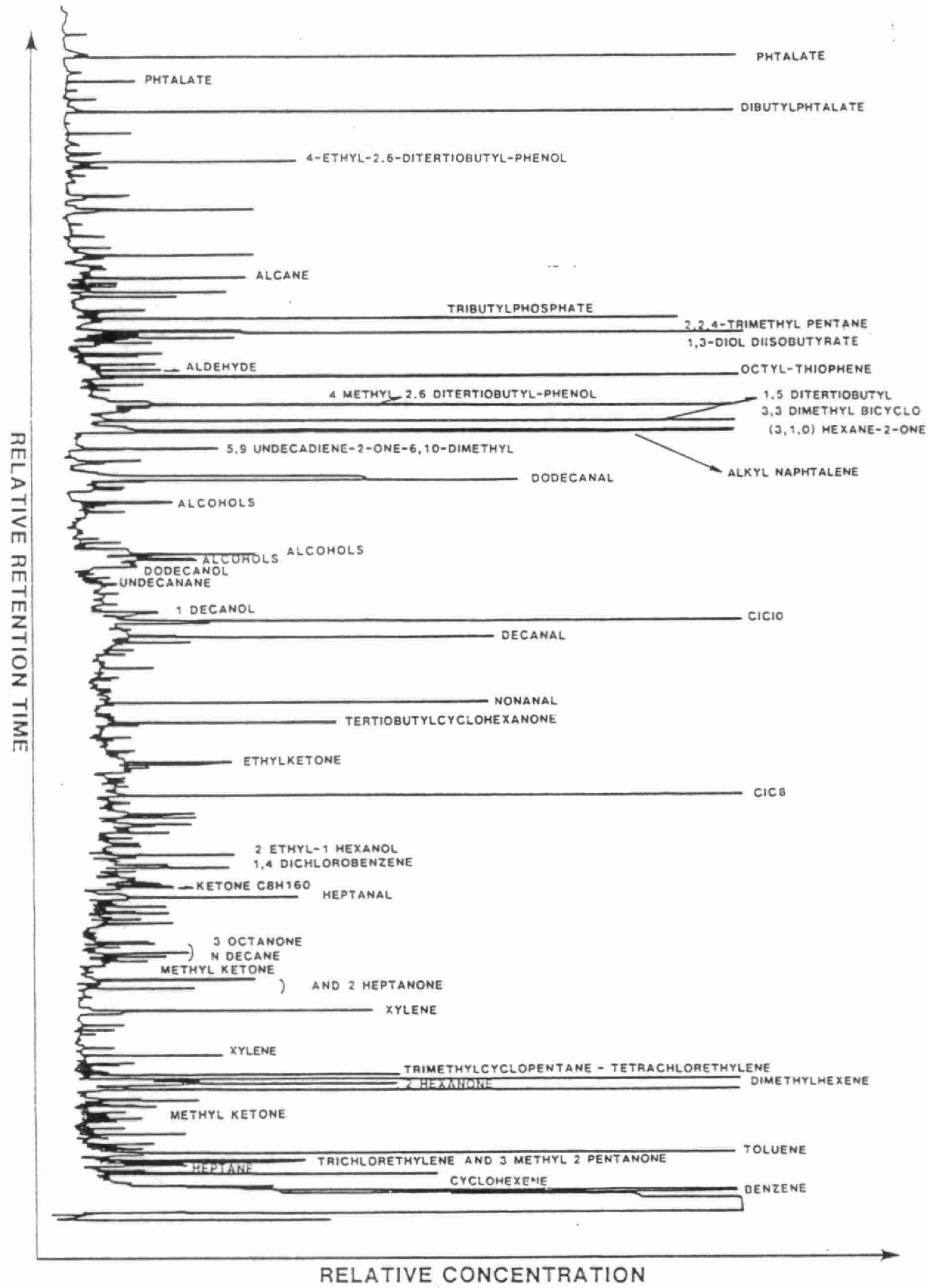

Figure 3. GC/MS Analysis of Section 2 Soak Water

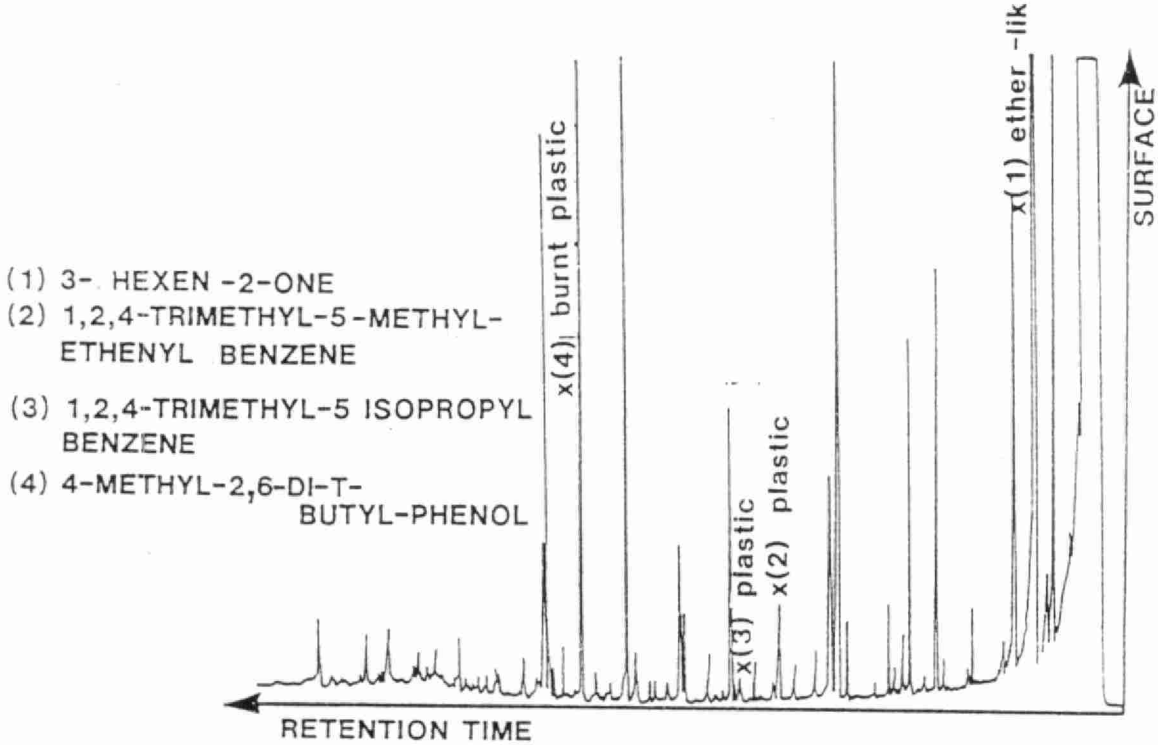

Figure 4. SDE Extract of Section 2 Soak Water GC/Odor Chromatogram

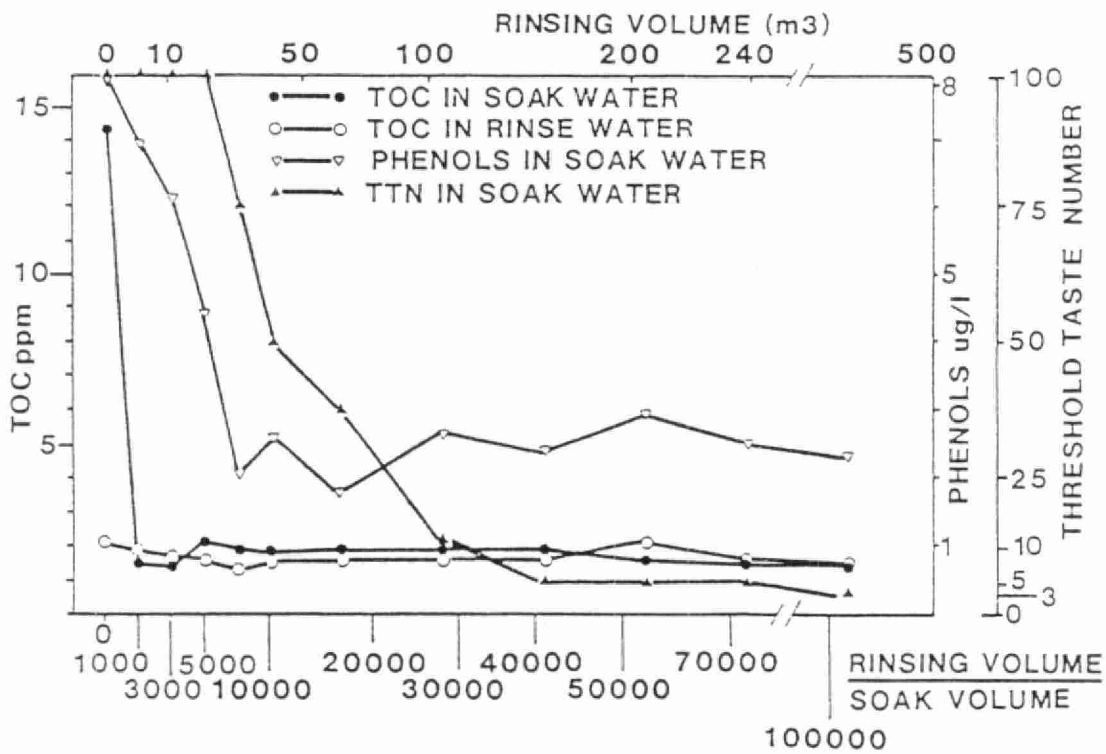

Figure 5. Evolution of Desorption Products in a Defective Polyethylene Pipe

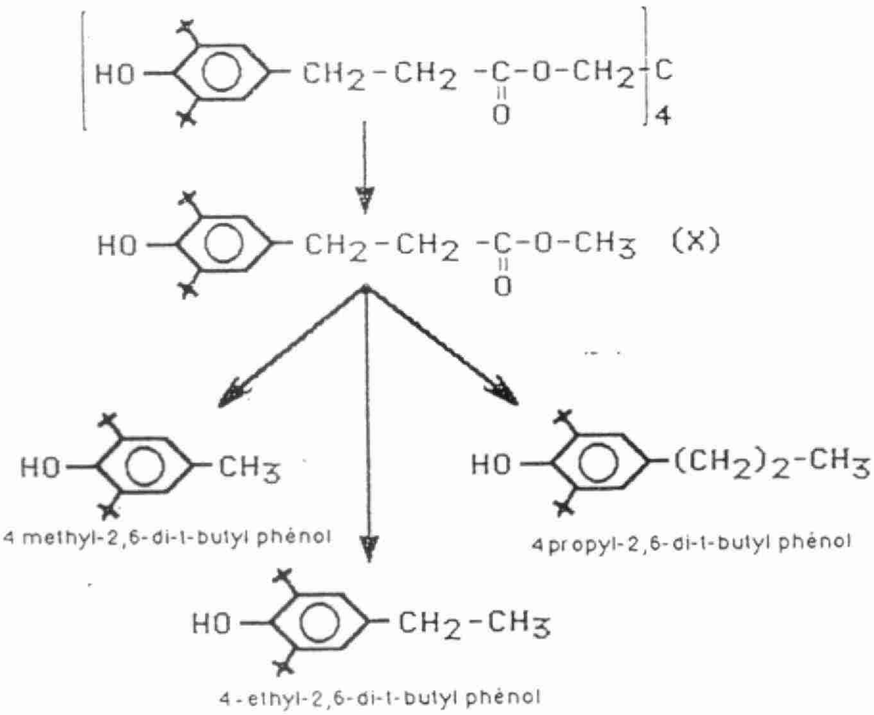

Figure 6. Degradative Way for Irganox 1010 Under Air Extrusion Conditions

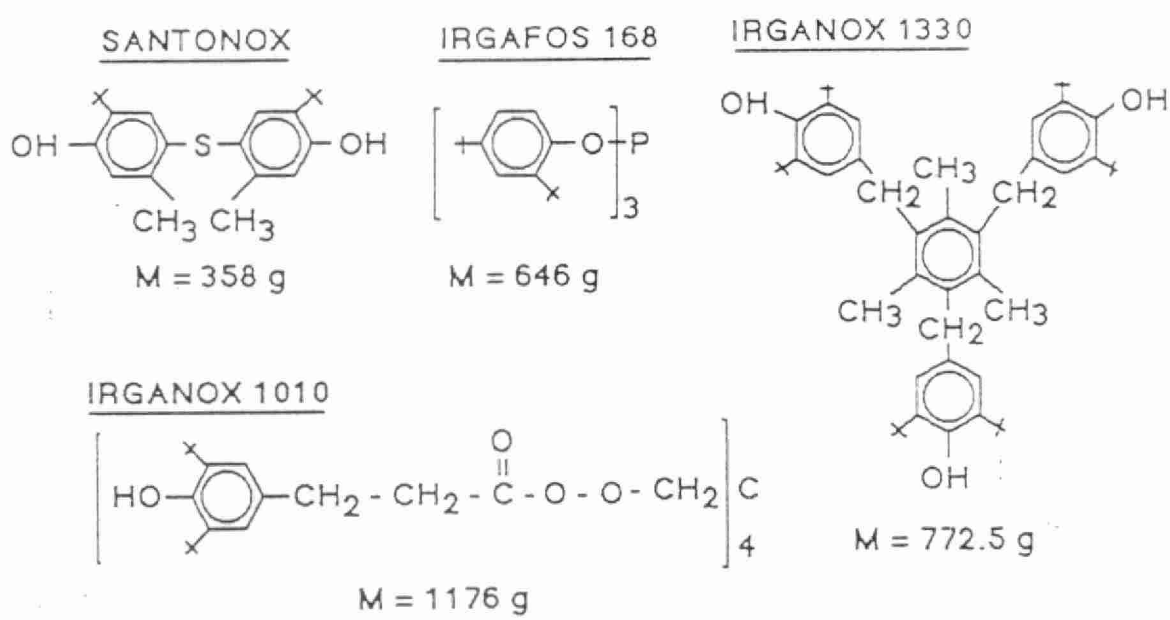

Figure 7. Example of some HDPE Antioxidant Additives

PROJECT DESCRIPTION

Project Title:

Use of Micronucleus Tests on newt larvas for the detection of mutagenic substances

Contact (name of person, organization, address, telephone):

Y.Lévi, Centre de Recherche de la Compagnie Générale des Eaux
Chemin de la Digue, B.P.76, 78600 Maisons-Laffitte, FRANCE(1 39 62 34 56)

Project Description (Please attach a schematic diagram if appropriate):

- The detection of mutagenic activities in water is made difficult by the various stages of pollutant removal and concentration. Moreover, the practice of tests on bacteria and mammal cells complicates the extrapolation of results.

- The Micronocleus test is applied to newt larvas (pluerodile) living in the water to be analyzed. After a period of incubation, a count is made of the number of hematites showing an abnormality of the micronucleus

- The test is applied to surface waters during treatment and, more especially, in connection with studies on the action of disinfectants. (chlorine, chlorine dioxide, ozone).

- Its use is also contemplated for the control of materials in contact with potable water.

Operating and cost data (including data on efficiency, results, etc.):

Place(s) of installation/application (including dates):

Center of Development Biology. Paul Sabatier University, Toulouse, France

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

Collaboration with Center of Developement Biology Paul Sabatier University, Toulouse, France

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

Mutagenesis vol.2 no.3 pp.211–214, 1987

Detection of mutagenicity in drinking water using a micronucleus test in newt larvae (*Pleurodeles waltl*)

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We have previously described a micronucleus test using erythrocytes from larvae of the urodele amphibians *Pleurodeles waltl* (pleurodele) and *Ambystoma mexicanum* (axolotl). The test is based on a comparison of the levels of micronucleated erythrocytes in blood smears from larvae reared in water containing a clastogen, with the levels from larvae reared in purified water. Using larvae from the pleurodele, we have employed this test to evaluate mutagenic activity in drinking water. Groups of larvae were reared in tap water, while control groups were reared in tap water which had been filtered over sand and active carbon to remove micropollutants. Seven separate tests carried out between October 1985 and May 1986 all gave positive results of varying degree depending on the time of year. This test is therefore able to detect clastogens in normal drinking water. It could be used for quality control of drinking water during the various stages in the treatment of raw water without any requirement for prior extraction or concentration of micropollutants.

Introduction

The potentially genotoxic substances in drinking water come from various sources. They may be mutagenic contaminants of the raw water (chemicals from industrial wastes, agricultural pesticides, domestic effluents, vehicle exhaust fumes, radioactive substances, etc.), but paradoxically they may also be organic mutagens produced during the treatment process itself.

The first examples of the latter type were the trihalomethanes detected in water treated with chlorine (Bellar *et al.*, 1974; Rook, 1974). Among these substances, chloroform has been found to be carcinogenic in experimental animals (National Cancer Institute, 1976).

Organic micropollutants in chlorinated water have given positive results in the Ames test, although the exact nature of the substances responsible has not been determined (Glatz *et al.*, 1978; Nestmann *et al.*, 1979; Loper, 1980; Cheh *et al.*, 1980; Grabow *et al.*, 1981; Grimm-Kibalo *et al.*, 1981; Zoetman *et al.*, 1982; Athanasiou and Kyrtopoulos, 1983; Kool *et al.*, 1984; Monarca *et al.*, 1985; Vartiainen and Liimatainen, 1986). Mutagenic activity has also been detected after treatment with chlorine dioxide (Zoetman *et al.*, 1982; Kool and de Kruijf, 1985), and even after treatment with ozone (Kool *et al.*, 1984; Van Hoof *et al.*, 1985).

Bacterial tests are not sufficiently sensitive to be used directly on samples of drinking water. To test for genotoxicity the micropollutants need to be concentrated before analysis. The composition of such extracts depends on the method of concentration. In fact, no extract contains the exact relative proportions of the various pollutants of the original sample, and the mutagenic effects of a given sample cannot, therefore, be accurately quantified using existing methods of sample concentration.

In order to get round this difficulty, various *in vivo* tests using fish have been proposed (Kligerman *et al.*, 1975; Prein *et al.*, 1978; Kligerman, 1979; Alink *et al.*, 1980; Hooftman, 1981; Hooftman and Vink, 1981; Hooftman and de Raat, 1982; Van der Hoeven *et al.*, 1982; Vigfusson *et al.*, 1983; Kligerman *et al.*, 1984; Van der Gaag and Van de Kerkhoff, 1985). Although some of these tests, especially those involving exchange of sister chromatids, can detect genotoxic activity in highly polluted surface water, they do not seem to be sufficiently sensitive for use on drinking water.

In previous studies (Siboulet *et al.*, 1984; Grinfeld *et al.*, 1986; Jaylet *et al.*, 1986a,b) we reported the use of a micronucleus test in two urodele amphibian species: *Pleurodeles waltl* (pleurodele) and *Ambystoma mexicanum* (axolotl).

Clastogens lead to the formation of micronuclei that are readily visualized in the red cells of larvae of both species. The micronuclei are seen as small intracytoplasmic clumps of chromatin which resemble small nuclei. They are formed from chromosome fragments or whole chromosomes that have not migrated to either spindle pole during anaphase. Micronuclei are thus due to chromosome fragmentation or to a disorder in the mitotic machinery. In the former case, the micronuclei are chromosome fragments with no centromere, unattached to spindle fibres. In the latter case, they consist of whole chromosomes which did not migrate to the poles, due to spindle defects. Clastogenic substances and spindle poisons both lead to an increase in the number of cells containing micronuclei.

Evans *et al.* (1959) were the first to suggest counting cells with micronuclei as a method for the evaluation of cytogenetic damage, and induction of micronuclei has been used subsequently by many workers to measure genotoxicity. A detailed description of the micronucleus test using bone marrow polychromatic erythrocytes from small mammals is given by Schmid (1976). Results from the micronucleus test and recommendations for its practical application have been surveyed by Heddle *et al.* (1983).

Erythrocytes in the larvae of the pleurodele and the axolotl are large, ovoid, nucleated cells (30 μm long) which divide actively in circulating blood. Micronuclei in these cells can be readily visualized on blood smears.

Under normal rearing conditions the spontaneous level of micronucleated cells is generally <10 per 1000. Comparison of the levels of micronucleated erythrocytes between larvae reared in pure water, and those reared in water containing a potential clastogen, provides a measure of the mutagenicity of the water under test, and can readily be applied to samples of drinking water.

Materials and methods

The test used pleurodele larvae. Two months after laying, they are ~30 mm long, and they then reach 40 mm within the next 10 days. This is a suitable time for taking blood samples by cardiac puncture. This represents a period of fast growth, and the number of mitoses in red peripheral blood cells is around 10‰

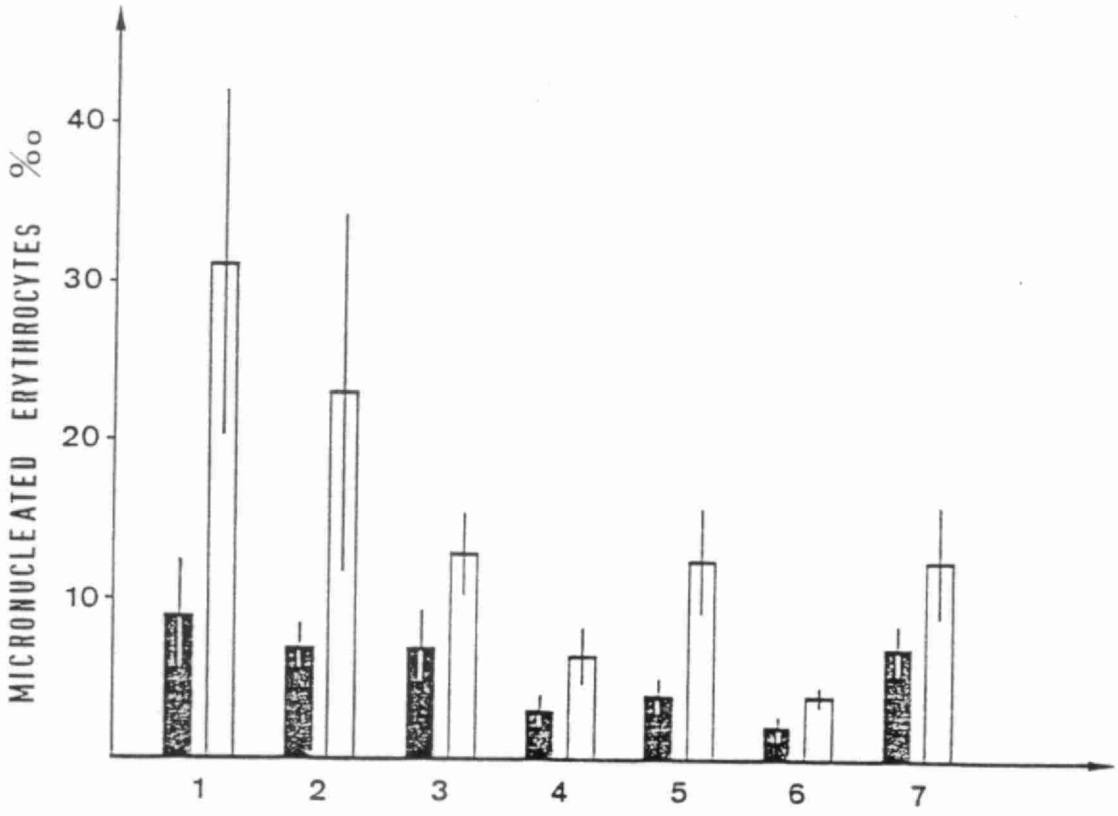

Fig. 1. Histograms of median values obtained for the various tests on laboratory drinking water samples. In black: tests using drinking water filtered over sand and carbon; in white: tests over the same period using non-filtered tap water. Error bars indicate 95% confidence limits. Date of tests: no.1: 12.10.85 to 24.10.85; no.2: 24.10.85 to 12.11.85; no.3: 04.12.85 to 16.12.85; no.4: 31.01.86 to 19.02.86; no.5: 04.03.86 to 20.03.86; no.6: 21.03.86 to 15.04.86; No.7: 17.05.86 to 23.05.86. Tests 1 and 3 were carried out in glass containers with daily changes of water. Tests 2,4,5,6 and 7 were carried out in running water aquaria.

Table I. Results of tests on laboratory tap water (expressed as the number of micronucleated cells per thousand)

DATE	12.10.85 to 24.10.85		24.10.85 to 12.11.85		04.12.85 to 16.12.85		31.01.86 to 19.02.86		04.03.86 to 20.03.86		21.03.86 to 15.04.86		17.05.86 to 23.05.86	
	Filtered tap water	Tap water	Filtered tap water	Tap water	Filtered tap water	Tap water	Filtered tap water	Tap water	Filtered tap water	Tap water	Filtered tap water	Tap water	Filtered tap water	Tap water
Lower extreme	2	14	4	5	1	5	0	1	0	4	0	2	0	2
Lower quartile	6.5	20	5.5	14	5	10	2	5	2	10	1	3	4	7
Median	9	31	7	23	7	13	3	6.5	4	12.5	2	4	7	12.5
Upper quartile	13.5	45	9	41	11.5	17	4	8	5	19	3	4.5	8	16.5
Upper extreme	21	64	15	105	20	29	7	15	14	36	4	12	12	42
Mean	10.5	34.3	7.4	31.41	8.68	14.1	3.1	7.2	4.1	14.7	2.1	4.3	6.05	14.05
Results		+		+		+		+		+		+		+
Animal number	10	13	15	17	19	19	10	10	20	20	20	20	20	20

The tests were carried out over the 8-month period between October 1985 and May 1986. Tests 1 and 3 were carried out in glass containers with daily changes of water and food. All the other tests were carried out in running water aquaria. Fresh food was added daily.
+ Positive result.

(Deparis, 1973). The details of the rearing of the animals and the methodology of the test have been described elsewhere (Jaylet *et al.*, 1986a).

Water samples were taken from a laboratory tap at the Paul Sabatier University in Toulouse (France). The waterworks which supplies the University abstracts raw water from the river Garonne with a daily production of ~6000–9000 m^3. The raw water is treated with lime and aluminium sulphite or ferric chloride depending on the time of year. After flotation and sand filtration, the water is disinfected with chlorine.

The mean monthly level of organic carbon ranged between 1.2 and 2.1 p.p.m. throughout the period of testing. Seven tests (numbered in chronological order) were carried out between October 1985 and May 1986. The shortest test was 6 days (no. 7). Test numbers 1.3 and 6 lasted 12 days, test number 5, 16 days, and test numbers 2 and 4, 19 days. In each test the levels of micronuclei were compared between larvae reared in tap water and control larvae reared in tap water that had been filtered over sand and activated carbon. The filter consisted of a metallic cylinder containing 500 l of sand and gravel in the bottom part and 500 l of activated carbon in the upper part. It operated at a maximum pressure of 1.5 bars, and a water flow of 4 m^3 per h.

The chlorine content of tap water ranged from 0 to 0.2 p.p.m. It should be noted that pleurodele larvae die within a few hours if the level exceeds 0.4 p.p.m.

In the first and third tests, the experiments were carried out in 5-l glass containers containing 2 l of water. The water was renewed daily. In the other five tests, the experimental chambers consisted of two aquaria (with an overflow) continuously supplied with water. One aquarium was supplied directly from the tap, while the other received water from the same source after it had been filtered through sand and activated carbon.

In all cases, the water temperature was maintained at 20 ± 0.25°C. The larvae were fed on chironoma larvae which were added daily.

Expression of results

For each blood smear, the number of micronucleated cells was counted in a sample of 1000 erythrocytes. The statistical method described by MacGill *et al.* (1978) based on medians, limiting values and quartiles was employed to analyse the results. The median of a sample ($n \geq 7$) is calculated, and the 95% confidence interval is expressed by

$$M \pm 1.57 \times IQR/\sqrt{n}$$

where M = median, and IQR = interquartile range. The difference between the medians of control and experimental groups is significant at the 5% level if the two calculated confidence intervals contain no values in common.

Results

The results are represented in Figure 1, and detailed in Table I. The median values for the various control groups varied from test to test. However, in all cases, the larvae reared in untreated tap water had higher levels of micronucleated erythrocytes than those reared in tap water that had been filtered and treated with active carbon.

Discussion

Using this test we detected clastogenic activity in all samples of tap water taken at different times throughout the year. Filtration over sand and active carbon was able, at least in part, to remove these pollutants since the larvae reared in the treated water always had lower levels of micronuclei.

For identical treatment periods (12 days for test numbers 1.3 and 6; 19 days for test numbers 2 and 4) the level of micronuclei varied at different times during the year. For the 12-day treatment period (no. 1) the maximum was in October, while for the 19 day treatment (no. 2) it reached a maximum in November. Two non-exclusive hypotheses can be proposed to account for these changes. Firstly, the quantity of micropollutants and the content and nature of organic matter in the raw water may vary throughout the year (depending on Garonne river level), and thus affect the composition of the tap water. Secondly, the quantity of chlorinated compounds produced by treatment with chlorine is known to be temperature-dependent (Rook, 1974). The level of some micropollutants may therefore fall in winter. The level of micronuclei in control animals also varied with the time of year, generally in a similar way to that of the experimental animals. This difference could perhaps be attributed to genetic differences between the groups, although this is unlikely. More probably, a small proportion of the clastogenic pollutants was not removed by the sand and carbon treatment. This was in fact confirmed on more detailed analysis (results not shown). This would explain why a similar pattern was observed for both the control and experimental groups over the year.

Apart from these mechanisms, there is the possibility that the effects observed were due to a chlorine residual (e.g. HOCl, OCl^-, NH_2Cl, etc.) which might have been removed in our filter along with the organic micropollutants. These chlorine residuals either on their own or after transformation in the organism could have been responsible for the clastogenic effect. For example, hypochlorite has been reported to cause osmotic fragility in blood cells in rats (Abdel-Rahman *et al.*, 1984), and chromosome damage in cultured cells (Ishidate *et al.*, 1984).

A further control would be to rear a group of larvae in 'ultrapure' water (deionized and devoid of all organic matter) to which essential salts and an amount of chlorine equivalent to that found in the tap water are added.

The aim of these studies was to discover whether the test was sufficiently sensitive to be used directly on samples of drinking water without prior concentration. To our knowledge this is the first description of a test using an aquatic vertebrate for the detection of potential clastogens in samples of tap water.

The test also gave positive results with raw water that was known to be polluted by factory effluents (unpublished results). This method for detection of mutagenicity in fresh water could therefore be employed for quality control of drinking water during the various treatment stages.

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PROJECT DESCRIPTION

Project Title:

Application of Data processing to remote control of potable waterworks and dependent networks.

Contact (name of person, organization, address, telephone):

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J.C.Arraudeau, Compagnie Générale des Eaux, 52, rue d'Anjou, 75008 PARIS, FRANCE (1 42 66 91 50)

Project Description (Please attach a schematic diagram if appropriate):

We mention some of the computerized projects set up at Compagnie Générale des Eaux :

- Computerization of paper work (book-keeping, cost analysis, salaries, inventories, office automation, etc...). Since 1980, there are been new developments as decentralization of terminals in local agencies and meter reading by portable terminal
- Computerization of technical management - are guided by the criteria : decentralization, hierachy and safety. Since the early seventies this is progressively materialized in the Paris suburban Utility with basic automatic systems at local level, production plant control rooms and finally overall coordination level (Water Movements Centre).
- Technical design. Drawing board work must give priority to the links between the extremely varied disciplines to be approached (civil engineering, chemical engineering, mains, electrical engineering). Starting from CAD equipment and software, experiments are currently in progress to set up highly sophisticated graphic information between systems.
- In-house communication based on videotex teletel and specialized data base consultation have recently been introduced and are rendering considerable service.

Operating and cost data (including data on efficiency, results, etc.):

- Nowadays a mini-automated controller can be fitted to each filter, the exchange of information being provided by a local plant network. Not only does the top heavy centralized system disappear, but an improved service is supplied to the operator, allowing highly flexible adjustment.
- Decisive parameters can be measured continuously downstream from the treatment plant, and different stages of the tratment and in the distribution system (flow meter, ammonia, TOC, Aluminium, Heavy metals, suspended solids levels, turbidity, residual chlorure sensors...) transmitting measurements to the CPU, make it possible to foresee all risk of pollution and changes in the quality of water.
- Based on the forecast conception for the next 24 hours, the "pilot" Expert System, developped in the treatment plants belonging to the Ile-de-France water board, enables to propose an operating sequence for the lifting and feeding equipment in keeping with the capacity of the reservoirs and to propose a planning for the washing of the filters.

Place(s) of installation/application (including dates):

Paris suburban Utility

Local Agencies of the Compagnie Générale des Eaux

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

COMPUTER TECHNOLOGY IN WATER DISTRIBUTION

Jean-Claude ARRAUDEAU, Jean-Louis DAVOUST, Olivier PASCAL

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The application of data processing in the water distribution trade is characterized by the pursuit of traditional objectives like increased productivity, enhanced quality of the service rendered with its implication of secure operating, optimization of investments and improved working conditions for the personnel. But the development of these applications must cope with certain specific factors:

- the opposition between the speed at which computer technology evolves and the necessarily progressive phasing in of the admissible changes. In fact, the water utility is obliged to respect continuity as its prime obligation and rely on an infra-structure that is only renewed at a slow pace:

- the scattered organization of widely-spaced water distribution systems:

- the great number of different technical and administrative techniques involved.

The fields in which data processing are applied is therefore extremely varied representing a vital challenge. Developments in computerization must be guided to form a coherent whole whereby the overall level of the service can reach objectives of productivity, quality and so on that justify each individual application.

This is perspective in which we would like to mention some of the computerized projects set up at Compagnie Générale des Eaux, analyzing the narrative of their development and gradual integration.

Computerization of paper work in such traditional fields as book-keeping and cost analysis, salaries, inventories, office automation, etc. In these areas the break-in of micro-processing has enabled small scale water utilities and local agencies of larger departments with self-sufficient and flexible tools, using software packages that can be adapted to the local background.

Administrative computerization in water management has a more specific character when it comes to subscriber accounting and billing. Towards the end of the sixties, the computer department of Compagnie Générale des Eaux, that issues several million invoices per annum, procured powerful central processing equipment and billing software

designed for its own use. Since 1980 there have been new developments:

- decentralization of terminals in local agencies.
- meter reading by portable terminal.

Computerization of technical management in potable water production plants and distribution networks enables all site to be centrally managed (including process operating, network operating and maintenance functions).

Three criteria guide systems designing: decentralization, hierarchy and safety. In the Paris Suburban Utility, these criteria are materialized at three levels that have been phased in gently since the early seventies:

- basic automatic systems at local level.
- production plant control rooms.
- overall coordination level (Water Movements Centre).

Coordination jobs use knowledge base systems (filter washing, centralized network hydraulic management).

Technical design. Drawing board work must give priority to the links between the extremely varied disciplines to be approached (civil engineering, chemical engineering, mains, electrical engineering). Starting from CAD equipment and software, experiments are currently in progress to set up highly sophisticated graphic information between systems.

Research and development Department. Operational research software is used here to draw up a plan of experience and analyze the results. It operates data acquisition loops, often intricate, mainly digital, for monitoring the treatment line and the network.

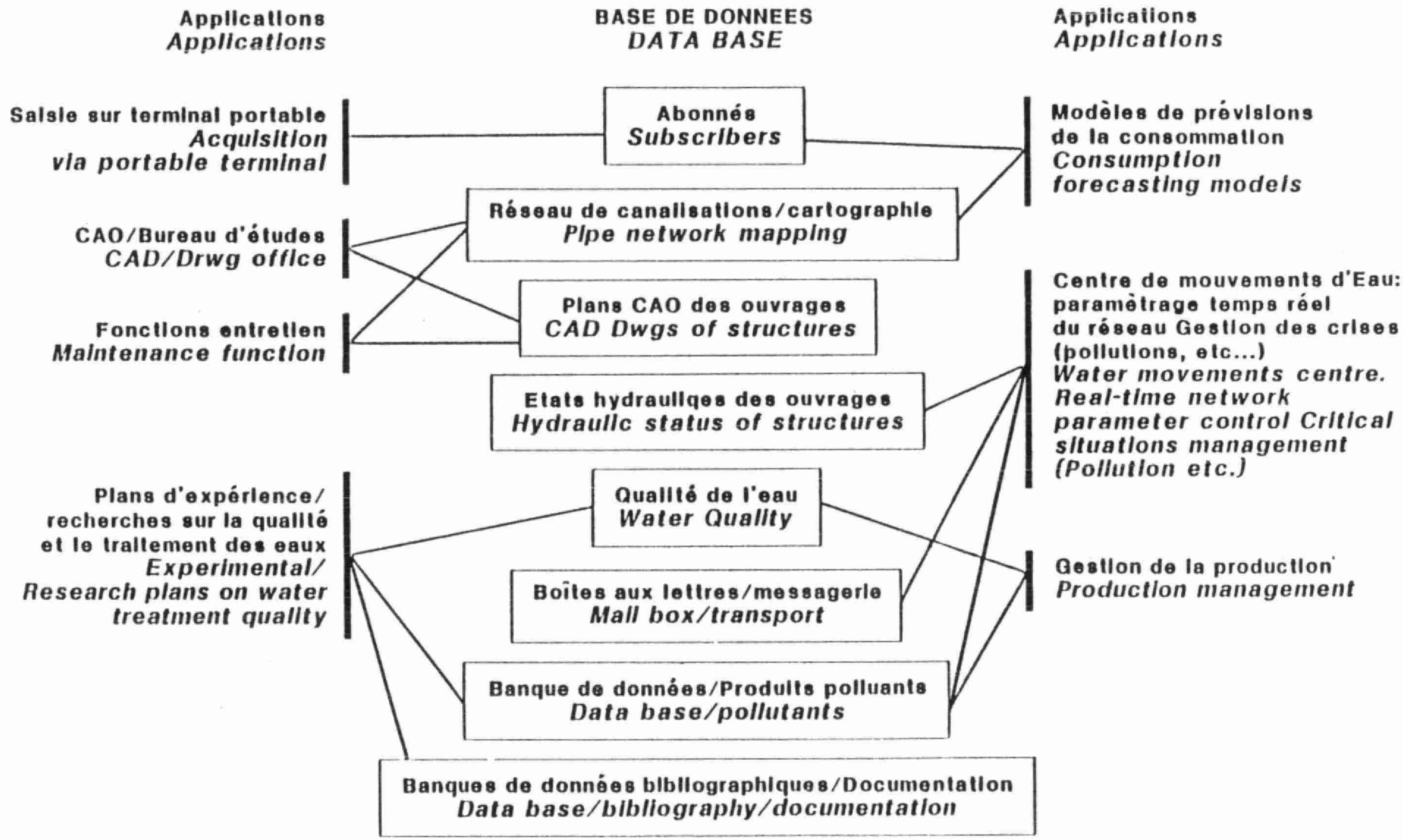
In-house communication. Often a difficult challenge for large-scale utilities, of which the structure is frequently decentralized. Computerized telecommunications, based on videotex, teletel and specialized data base consultation, have recently been introduced and are rendering considerable service.

Independent developments between different sectors of application have enabled quick progress to be made without having to upset the general strategy of the company, and allowing time for workers to adapt to the new structures.

The need for a more global approach to computerization is becoming more and more apparent. It is made possible by high performance tools and data base management systems that play the part of a turntable between the various applications made difficult by the insufficient standardization of data processing products.

A data-processing plan, regularly appraised and adapted maintains organizational vigilance and steers the individual developments towards the general objectives.

Exemples de bases de données polyvalentes pour une distribution d'eau
Examples of multi-purpose data bases for a water distribution system



PROJECT DESCRIPTION

Project Title:

Development of Tasting Assistance Automatons for the "UP AND DOWN" Testing Procedure.

Contact (name of person, organization, address, telephone):

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Project Description (Please attach a schematic diagram if appropriate):

- Development of an automaton designed to : dispense water samples to tasters, effect the dilutions resulting from the test responses, process, print and store the results.

- The up-and-down procedure requires the distribution of several samples to an untrained tasting panel, for tasting in pairs or for triangular testing. The fact that these tests take place in the waterworks makes the use of a fully automatic system indispensable.

- The automaton combines three units :
  - water dispenser,
  - input/output management unit
  - control and operating computer and peripherals

- The use of this system is being generalized to all Compagnie Générale des Eaux potable water production plants for quality control.

Operating and cost data (including data on efficiency, results, etc.):

Place(s) of installation/application (including dates):

- Research Center, Maisons-Laffitte since 1986.

- Choisy-le-Roi Waterworks (Ile-de-France water board and C.G.E.) 1987

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

PROJECT DESCRIPTION

Project Title:

Expert system to control the treatment process in order to avoid taste and odor problems.

Contact (name of person, organization, address, telephone):

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Project Description (Please attach a schematic diagram if appropriate):

Statistical methods have been developed to understand and resolve the problems associated to unpleasant tastes and odors in drinking water (Anselme, Bordet, Mallevialle, AWWA 1986). These models allow to estimate both the organoleptic qualities of water from the corresponding chromatographic profile and the chromatogram from the flavor profile. Encouraging results obtained with these models have led to the long-term goal of controlling the treatment process to avoid taste and odor problems. But all the problems associated with tastes and odors cannot be resolved exhaustively. A correct interpretation of the results given by the model requires a full investigation of the model (direct and inverse) and its limits. That is why the know-how of the statistician analyst is required. When the compounds responsible of tastes and odors problems are identified, it is again heuristic methods which are used to determine the treatment solutions. The natural extension of the study consists in considering the different techniques of Artificial Intelligence in order to realize an integrated system including algorithmic and heuristic methods.

The long-term objective is to implant the expert system in the treatment plants. This expert system would have to permit the water distributors to solve a lot of problems without the need of a physico-chemical analysis and to modify some aspects of their normal operation to alleviate taste and odor problems. However, to realize this long-term goal a reference data base must be collected. This data base consists of water samples taken in different treatment plants for which GC/MS analyses and flavor profiles are encoded and stored.

Functional Specifications

This expert system is composed of several modules. Each module was developed in an independent way, but in the inclusive system all of them are in interaction.

Module of Information Retrieval
The purpose of this system is to provide the user an intelligent assistance on the retrieval of information concerning the taste or odor and the taste or odor threshold of a certain chemical compound from available information bases.

Module of Guiding Simulations Made by the Stochastic Model
Relationships between flavor profiles and chromatograms are often unknown. The identification of the compounds responsible of unpleasant tastes and odors is difficult. They are present at very low concentrations and show interaction mechanism (synergetic effect). In these cases, the expert can use a stochastic model.

Module of Choice of Treatment Solutions
When the compounds responsible of unpleasant tastes and odors are identified the expert system has to propose some solutions of treatment to eliminate them in regards to treatment lines constraints. Then, the expert system tests the validity of the proposed solutions using transfert functions of each treatment step.

Place(s) of installation/application (including dates):

Expert system prototype already available at the
Lyonnaise des Eaux Research Center (1988)

Patent staus, if applicable:

\-

Other information (e.g., funding source, cooperating agencies, etc.):

See display material to be available at conference.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

EMERGING WATER SUPPLY TECHNOLOGY AWWARF Code #: FR-12

PROJECT DESCRIPTION

Project Title:

Immunology in fast automated water analysis

Contact (name of person, organization, address, telephone):

M.M.Bourbigot, Centre de Recherche de la Compagnie Générale des Eaux
Chemin de la Digue, B.P.76, 78600 Maisons-Lafffitte, FRANCE (1 39 62 34 56)

J.Mallevialle, Centre de Recherche de la Lyonnaise des Eaux,
38, rue du Président Wilson, 78230 Le Pecq, FRANCE (1 39 76 64 10)

Project Description (Please attach a schematic diagram if appropriate):

Immunotests are based on the fact that the antibodies generated by an animal to defend itself against a given bacterial infection, for instance, reach specifically with these antigens that caused their synthetisation. The serum containing these antibodies can as a rule be used therefore to fix or to detect the corresponding microorganism.The application of these techniques to potable water gives rise to a number of problems :

- many of them need heavy equipment
- they are mainly designed to measure large concentrations and the signal to background noise ratios ar far from being optimized
- They are only utilizable as it is possible to obtain antibodies that are on a sufficient specific scale and in ~~re~~productible form.

The monoclonal antibodies bring a solution to the last difficulties mentionned.

In the light of the overall research, our approach selected is based on the obtention of one monoclonal antibodies capable of specifically recognizing E.Coli with a response time of two hours. A single bacterium in a 100 ml sample must be detectable with a maximum of reliability

Operating and cost data (including data on efficiency, results, etc.):

We have obtained a specific monoclonal antibodies but extra research is still needed in order to optimize the signal. Unmistakable distinction between live and extract bacteria must be verified.

Place(s) of installation/application (including dates):

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

Compagnie Générale des Eaux, Société Lyonnaise des Eaux and the Société des Eaux du Nord and l'INSERM (Lille) work together to design systems based on these techniques. The research is patronized by the Health and Environment Ministry together with the Agence de Bassin Seine Normandie.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

ITALY

ITALY

EMERGING WATER SUPPLY TECHNOLOGY

AWWARF Code #: IT-01

PROJECT DESCRIPTION

Project Title:

Utilization of Special Steels for the E.U.R. Raising Water Reservoir

Contact (name of person, organization, address, telephone):

A.C.E.A. Servizio C.I.I.O.E.
Ing. Paolo Nervi
00100 ROMA piazzale Ostiense, 2
ITALY

Project Description (Please attach a schematic diagram if appropriate):

See Attached Project Description

Operating and cost data (including data on efficiency, results, etc.):

total cost 21,000,000,000 lire

capacity: 1,700 m3

max. discharge 3.9 m3/sec

Place(s) of installation/application (including dates):

ROMA - ITALY

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

UTILIZATION OF SPECIAL STEELS FOR THE E.U.R. RAISING WATER RESERVOIR

The structure is composed of a water collecting basin placed at 85 m from the ground, of a hanging toroidal tank and of a piezometric cylindrical tower. All these units are supported by tubular structures with inlet/outlet water pipes, stairs and elevator passing through.

The structure is made of special steel which guarantees the achievement of the following purposes:

- valorization of the structure shape: being it visible from many quarters of the city, the use of such a material allows a close connection between functionality and aesthetical needs;
- long life: being the structure subjected to high thermal variations and to condensate phenomena, maintenance works will be considerably reduced.

The steels employed are of IT-ACOR 2 (ITALSIDER corrosion proof) and RESCO 36 SB (AFL FALCK) type. Both the steels present similar performances at COR-TEN (Corrosion resistance and tensile strength) B type.

These steels are killed, ferritic-pearlitic structured and belong to the so called "weathering steels" (weather corrosion proof).

The use of such materials, replacing the traditional carbon steels, allows remarkable thickness reductions with the consequent weight decrease.

The steels contain an amount of about 1-3% of copper alloy, chrome, nickel, vanadium or niobium and phosphorus. Their weather corrosion resistance is higher than the one of similar unalloyed steels.

Their improved anti-corrosion performances are due to the oxidation substances built up on the steel surface which create a tough and adherent protective layer consisting of a complex system of oxides and salts (autopassivazione): thickness loss is reduced and structure life increased.

Further remarkable properties are:

- high yield point;
- weathering resistance four to five times higher than the usual structural grade carbon steels;
- good weldability with the usual welding processes.

Although these materials can be conveniently used as uncoated, the painting of the parts in direct contact with the water (some oxides are water soluble) and of the external structure (to ensure a longer life to the same) has been provided for.

Several destructive and not destructive tests, according to precise and severe verification programs and to the rules in force, have been carried out.

By employing up-dated instruments, controls on the surface preparation by means of "white metal" and "semi-white metal" sandblasting with abrasive shots have been also carried out in order to obtain the surface roughness grade suitable for the protective paint coat adhesion.

During the production phases, particular attention has been paid to the controls on the paint films thickness: performance tests in "saline fog chamber" have been realized on samples.

Moreover, it must be pointed out that about 4/5th of the whole external surface of the structure are coated with low carbon austenitic stainless steel, corresponding to classification UNI X2 - Cr Ni 1811 (AISI 304 L).

This not adherent coating creates a ventilated air space: thus direct insolation is avoided, the underlaying structure is protected and aesthetical needs achieved.

To avoid corrosion, due to galvanic contact, the inox coating will be protected with an adequate system of insulating materials.

EMERGING WATER SUPPLY TECHNOLOGY

AWWARF Code #: IT-02

PROJECT DESCRIPTION

Project Title:

Tests Carried Out at the Waste-Waters Treatment Plant of Roma-Ostia to Improve Treatment Processes

Contact (name of person, organization, address, telephone):

Dott. Capuani - ing. Galeazzi
Depuratore di Roma - Ostia
via dell'Appagliatore
ROMA - OSTIA LIDO

Project Description (Please attach a schematic diagram if appropriate):

See Attached Project Description

Operating and cost data (including data on efficiency, results, etc.):

Place(s) of installation/application (including dates):

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

Department of ROMA/OSTIA Rome, 28.01.88

TESTS CARRIED OUT AT THE WASTE-WATERS TREATMENT PLANT OF ROMA/OSTIA

Injection of aluminium polychloride and anionic polyelectrolyte

During the primary treatment, the injection tests of aluminium polychloride and anionic polyelectrolyte have been carried out several times in order to increase the primary efficiency: the necessary maintenance works of the secondary tank, in fact, led to drain the primary outlet effluent (totally or just in part) from the plant.

The figures relevant to the last testing period, from October 10th to 30th 1986, show an increase of the primary efficiency of about 20%, both as SST and COD, as to the primary efficiency results obtained in 1986 from October 1st to 10th.

The proportion of ingredients was about 20 ppm and 0,5 ppm, according to the flow rates treated respectively with aluminium polychloride (Prodefloc AC 190 - PRODECO) and anionic polyelectrolyte (A 4515 - PRODECO).

Tests with activated carbon powders

The tests carried out with activated carbon powders, directly injected into the secondary tanks (starting date: May, 27th 1987), have been decided on the need of improving

the aptitude of the activated sludge, placed in the plant biological sectors, to sedimentation. The purpose was that of obtaining a final effluent without sedimented solids and therefore presenting low analytical values.
The results achieved, with a dosage of about 100 kg/day of activated carbon powders, cannot be considered as complete since, after a first improvement of the sludge features, a flotation phenomenon of the same sludge into the sedimentation area occurred.

EMERGING WATER SUPPLY TECHNOLOGY AWWARF Code #: IT-03

PROJECT DESCRIPTION

Project Title:
New Integrated Process (Bacteria-Biocatalyst) Adapted to Pre-Existent Biological Plants

Contact (name of person, organization, address, telephone):
Dott. GASBARRO Mariella (ACEA) P.le Ostiense, 2 - 00154 ROMA

Prof. BLUNDO Roberto Ph.D. (ECOBIOS) Via Gravina di Puglia 26-00133 ROMA
tel. 6152346

Dott. GENTILINI Franco (ACEA) idem address

Dott. De Giuli (ACEA) idem address

Project Description (Please attach a schematic diagram if appropriate):
This new biotechnology is aimed at optimizing the management of under-sized or bad-working treatment plants, with the following advantages:

1) Reduction (about 50%) of BOD5 and COD

2) Reduction of about 1/3rd of the total sludge volume

3) Reduction of nauseating smell

Operating and cost data (including data on efficiency, results, etc.):

Continuous Flow Biocatalist: about 150 l/h 50 l/sec. of inlet sludge

Sea Bacteria: one inoculation per week (100 pounds/4000 m3)

Cost: From 10 to 30 liras per treated m3 (small and big sized plants) integrating plant, personne, raw materials, etc. included.

Place(s) of installation/application (including dates):

TOR BELLA MONACA (ROMA) VIII District

Starting date: From September 28th, 1987 up to now

Patent staus, if applicable:

Yes, patent pending.

Other information (e.g., funding source, cooperating agencies, etc.):

The integrating plant (Digester and biocatalist) is financed by ECOBIOS with an expense participation of ACEA.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

MICROBIOLOGICAL PROCESS AT THE TOR BELLA MONACA WASTE-WATERS TREATMENT PLANT

ECOBIOS microbiological process, started at the Tor Bella Monaca waste-waters treatment plant on September 27th, 1987, consists in injecting lipolytic and proteolytic bacteria together with a continuous flow product (a biocatalyst with a flow rate of about 150 l/h) directly into the aeration tank (the frequency of operations is foreseen by ECOBIOS).

Up to October 30th, 1987 the treatment has been carried out in the tank n.1; subsequently, starting from the same date, the inoculation was transferred to the aeration tank n.2.

The analytical results recorded do not appear so remarkable because of the very short testing period (1 month for tank 2 and 2-3 months for tank 1) and the bad working conditions. It must be taken into account that, not being it a pilot plant particular working conditions occurred (sudden damages of the turbines, bridge-crane stops, unavoidable injections of anomalous sludge into the tank) which created an unfavourable situation to control the process and to achieve the expected results.

Up to now, remarkable improvements of the plant treatment capacity have not been pointed out as it appears from the control parameters, which were very similar to the ones of the last testing period.

A positive figure is the sludge volume index (SVI): in

the experimental tank the values recorded were lower than the ones of the untreated tank.

A further figure to be stressed is the gradual reduction of foam during the treatments.

In conclusion, the carrying out of a research program about the utilization of more suitable structures (i.e. pilot plant) and of finalized analytical controls, in order to better verify the real positiveness of the product injection, is suggested.

RITORNARE ENTRO IL 15 GENNAIO 1988 A: FEDERGASACQUA
P.zza Cola di Rienzo, 80
00192 ROMA RM

EMERGING WATER SUPPLY TECHNOLOGY

AWWARF Code #: IT-04

PROJECT DESCRIPTION

Project Title:

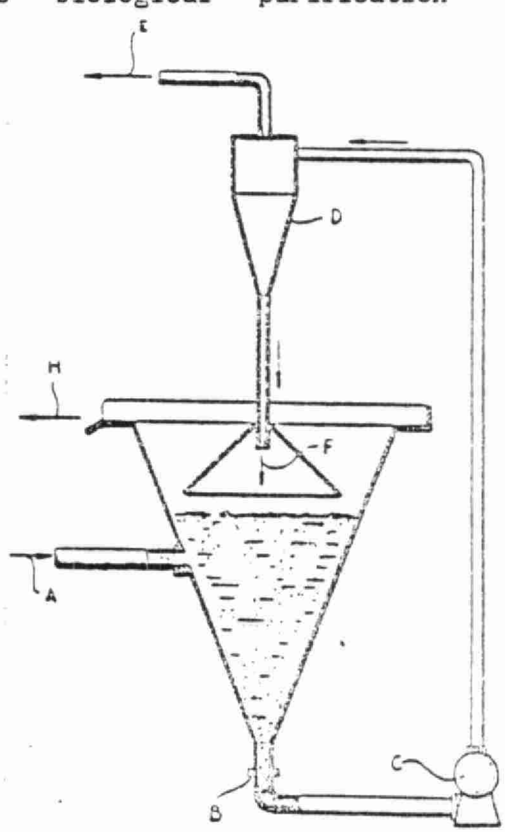
PROCESS FOR THE CLARIFICATION OF WATER

Contact (name of person, organization, address, telephone):

ING. GIORGIO MERLO
DIRETTORE GENERALE
AZIENDA ACQUEDOTTO MUNICIPALE DI TORINO
CORSO XI FEBBRAIO 14 - TORINO (ITALIA)
TELEF. 011/2615 TELEX 221644 AAM TO I

Project Description (Please attach a schematic diagram if appropriate):

In the process for the purification of water by flocculation a porous granular material, preferably constituted by pyroclasts, is used as decantation accelerator and can act as a substrate for a bacterial growth which achieves biological purification together with the chemico-physical purification of the flocculation. The drawing shows an application of the project to a clarifier of the fluidised-bed CYCLOFLOC ® type. Raw water is supplied at A together with aluminium polychloride and granular material constituted by porous pumice with particle sizes from 20 to 200 microns and a surface area less than 200 m^2/g. The sludge resulting is discharged at B and fed to a hydrocyclon separator which recycles at F granular pumice. Clarified water is extracted at H. The water to be purified must have an high oxygen content and a constant pH value not far from 8 and must not contain chlorine residual.



Operating and cost data (including data on efficiency, results, etc.):

The project achieves efficient T.O.C. and turbidity removal with much smaller amounts of flocculant than in a normal flocculation process.
Moreover the utilization of pumice eliminates the need of adding weighting agents such as sodium alginate.
The consequence is an improvement in the quality of treated water and considerable savings amounting to about 20% of the total treatment cost necessary for drinking water treatment.

Place(s) of installation/application (including dates):

The project has been experimented and implemented in the Cyclofloc basins of the treatment plant of the Po River water, in Turin, that has started operating in 1983. This plant belongs to the Azienda Acquedotto Municipale di Torino and supplies about 20% of potable water to the City of Turin with a flow capcity of 1500 l/s..

Patent staus, if applicable:

INVENTOR: DR.LUIGI VERDE -LUNGO PO ANTONELLI, 7- TORINO (ITALY)
ITALIAN PATENT N° 67303-A/85 (27.3.85)-N° 67520-A/85 (5.6.85)
U.S.A. PATENT N° 4.675.112 Date Jun. 23. 1987
FRENCH PATENT N° 8604272 Date March 25. 1986

Other information (e.g., funding source, cooperating agencies, etc.):

Information about the project has been given in a rapport presented at I.W.S.A. Congress in Amsterdam 15/19 Sept. 1986 about "advanced techniques in potable water treatment".

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

EMERGING WATER SUPPLY TECHNOLOGY AWWARF Code #: IT-05

PROJECT DESCRIPTION

Project Title:
APPARATUS FOR BIOLOGICAL MONITORING, WITH AUTOMATIC ALARM SIGNALLING

Contact (name of person, organization, address, telephone):

Francesco Di Paolo
A.C.E.A. (Rome City Electricity and Water Board)
Servizio Trattamento Acque Reflue
P.le Ostiense 2,
00154 Romas
tel. (Rome) 822802

Project Description (Please attach a schematic diagram if appropriate):

Electronic apparatus has been prepared for checking the behaviour of 3 rainbow trout kept separately in 3 plexiglass tanks with a continuous flow of water.

An electric field was generated at one end of each tank, with voltage charges; this sets up a disturbance area where each rainbow trout will only rarely venture.

When toxic substances are present in the water, this behaviour will undergo some variation, with frequent incursions into the electric field area, (state of agitation) or staying permanently in that area (state of inability to swim). Infrared ray barriers together with appropriate digital circuits have the task of collecting and memorizing these conditions and, by comparing the behaviour of the 3 rainbow trout, producing a state of alarm.

This state of alarm, sent to the control room, will indicate probable water pollution, thus permitting appropriate measures to be taken before it spreads.

The apparatus described above is a prototype made with the aim of improving water quality control carried out at certain points on A.C.E.A.'s water network.

The programme is being carried out with the construction and installation of a total of 10 pieces of apparatus. The normal chemico-physical characteristics of the water in the above control system are as follows: temperature (5+18)°C, Ph (6.5+8.5), dissolved oxygen 6m·/l, ammonia 0.01 p.p.m., chlorine 0.05 mg/l.

Operating and cost data (including data on efficiency, results, etc.):

During an experimental running period of 6 months, the apparatus has not given rise to any irregularities; some toxicity tests carried out have given the following results:

Chlorine = 1.5 mg/l - Alarm time: 20 mins.

Ammonia = 50. mg/l - Alarm time: 27 mins.

Soda = 1500 mg/l - Alarm time: 10 mins.

The biological monitoring apparatus consisting of rack, electronic circuits, mechanical apparatus and plexiglass tank, costs about 20,000,000 lire.

Place(s) of installation/application (including dates):

The prototype, after an initial trial period, has been installed at the A.C.E.A. centre at Via Cassia km.14.5 (Peschiera Aquaduct) since 1st September 1987.

Patent staus, if applicable:

Application for a patent has not been envisaged.

Other information (e.g., funding source, cooperating agencies, etc.):

See the information enclosed on a separate sheet.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

ADDITIONAL TECHNICAL NOTES

SUBJECT: Biological monitoring of Rome aqueducts by means of automatic alarm signals on control panel in control room.

A specimen of rainbow trout is placed in a narrow perspex tank with a continuous flow of water. An electric field is set up at one end of the tank. The particular arrangement of the electrodes and force lines of the electric field oblige the trout to flee from the area where the field is to be found.

The above-mentioned field is caused by a train of voltage impulses lasting for 15 seconds, repeated at regular intervals, as well as occurring every time the trout enters the area between the electrodes.

Under normal conditions, and in the "safety zone", the trout will rarely enter the electric field, and if this were to occur, it would immediately be localized by a barrier of infrared rays. Such an event is recorded in an electronic memory.

If there are any toxic substances in the water, this behaviour is subject to variation. In particular, the

intolerance reaction or the condition of uneasiness force the trout to keep on trying to enter the area subject to the action of the electric head, by which, however, it will be rejected again.

This event will occur several times over a brief period of time, and so the unusual behaviour of the fish will be analysed by digital electronic circuits that will trigger off an alarm situation.

Another alarm situation arises when the trout stays in the field for a long time. In Fig. 1, it is possible to see all the electronic apparatus's functions. Each photoelectric barrier comprises 8 receiving and transmitting channels operating in a multiplexer, where I.R. photoiodic transmitters (L = 940nm) are optically coupled with silicon phototransistors.

The photoelectric barrier A, with its interruption, permits the setting up of the electric field, and the acquisition of the translation memory of the incursion into the area defined by the electrodes (Fig. 2).

By means of a parallel-series transformation, the bits are transferred from the shift-register to a meter and then analysed.

At fixed intervals the pulsating circuit emits a train of impulses whose frequency, duration and range may be changed.

The photoelectric barrier B and a monostable multivibrator collect the evidence of the trout's presence in the electric field for a longer period than usual (the trout's total inability to move or its death).

The above remarks refer to only one control channel and one fish.

In order to avoid alarm signals deriving from causes other than the presence of toxic substances in the water (false alarms), the system comprises three channels in the complete apparatus (fig. 3).

The data are transmitted by optical couplers to a network with AND/OR operators.

This apparatus may be planned and it is possible to create the conditions for a particular alarm situation on the basis of known experiments and the required sensitivity.

The alarm signals are transmitted by means of a telecommunications vector to a central control room that will trigger off the existing emergency system.

IT-20

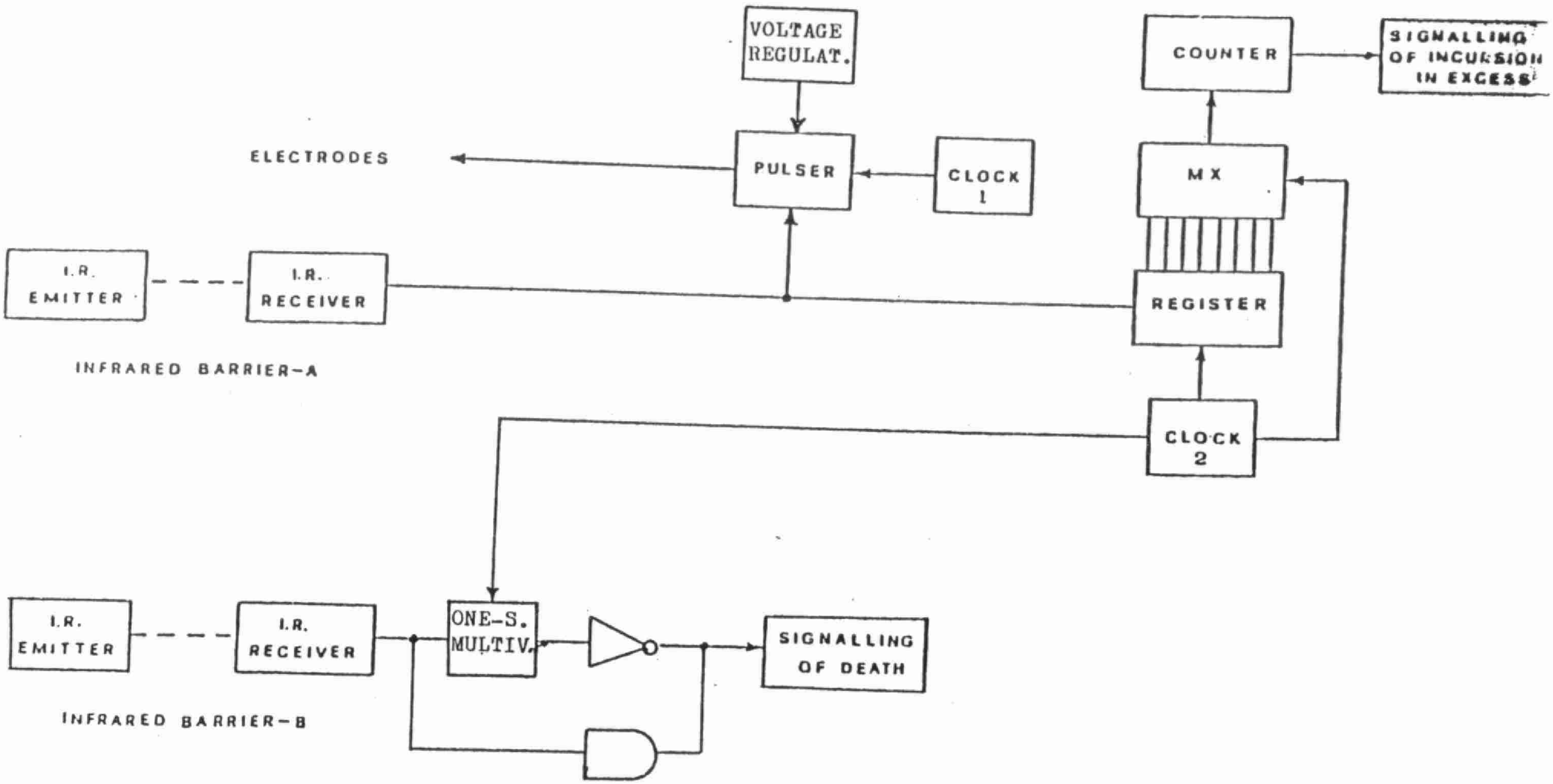
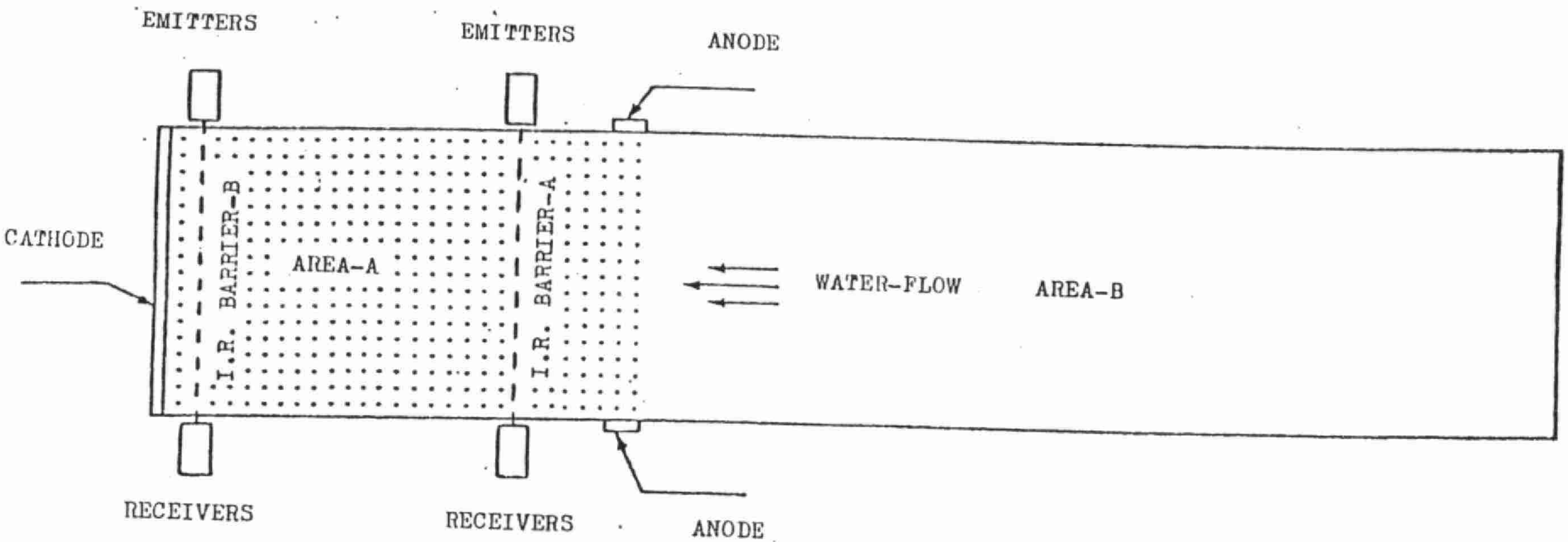

VOLTAGE REGULAT.
COUNTER
SIGNALLING OF INCURSION IN EXCESS
ELECTRODES
PULSER
CLOCK 1
MX
I.R. EMITTER
I.R. RECEIVER
REGISTER
INFRARED BARRIER-A
CLOCK 2
I.R. EMITTER
I.R. RECEIVER
ONE-S. MULTIV.
SIGNALLING OF DEATH
INFRARED BARRIER-B

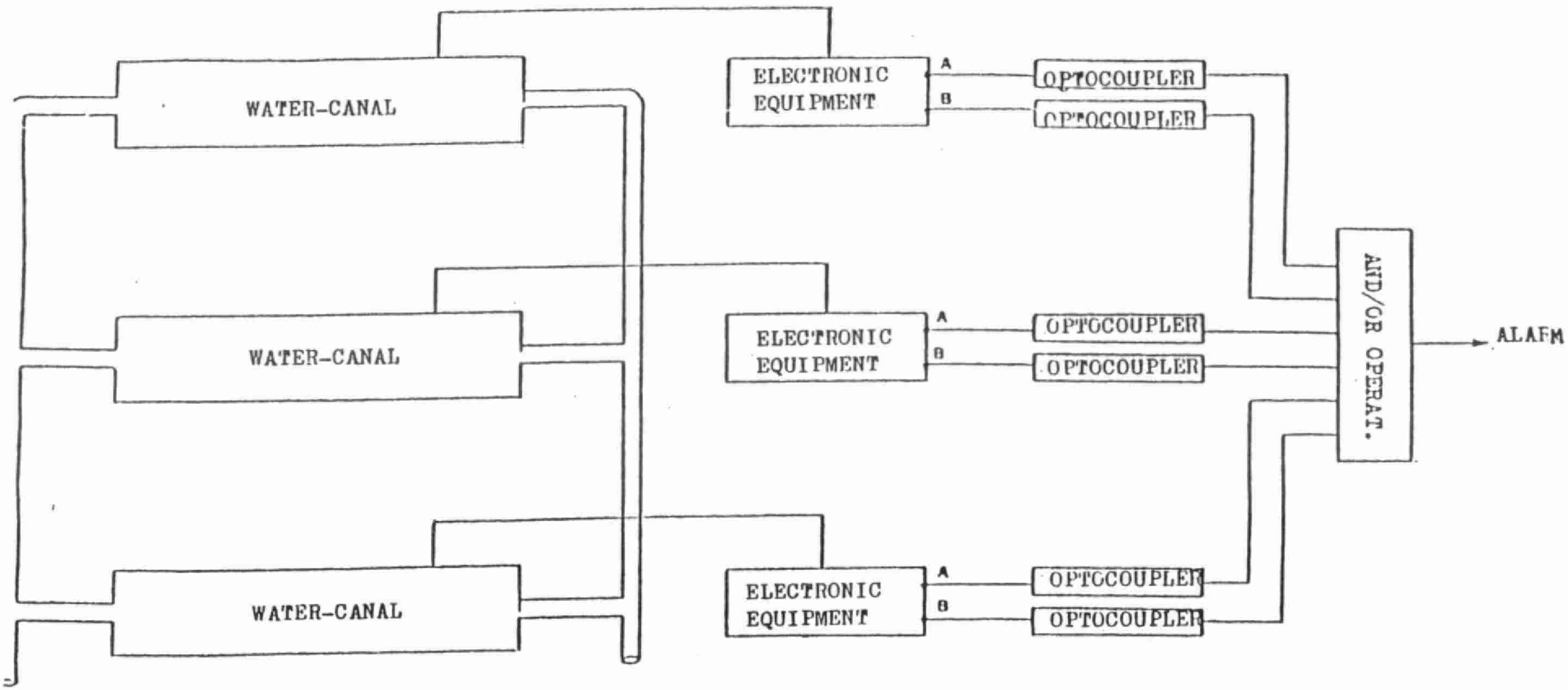
FIG. 1



AREA-A = AREA OF ELECTRIC FIELD

AREA--B = SAFETY AREA

FIG. 2



A = SIGNALLING OF INCURSION
B = SIGNALLING OF DEATH

FIG.3

IT-22

PROJECT DESCRIPTION

Project Title:

Level and Flow Syphon Device in a Sand Filtration Plant

Contact (name of person, organization, address, telephone):

A.M.G.A. - Via Venezia 1 - 48100 RAVENNA
Telex 583453 - Telefax 0554/34761 - Telefono 0554/39248
Ing. Luciano Moruzzi - Manager

Project Description (Please attach a schematic diagram if appropriate):

Most sand filtration plants are equipped with a syphon regulator device that insures a constant level of water on the filter by modulating as the sand filters become clogged. When all the filters are working in parallel, the syphon regulator device keeps the total rate of flow from all the filters more or less constant even if there is irregular loading of each filter unit. Because of this uneven filtration capacities after a backwash sequence, some filters become prematurely clogged. In order to prevent this uneven filter loading, a special modulating float value that is hydraulically operated and diaphragm actuated has been developed. It is controlled by an auxiliary pressure differentiated of approximately 2 bars through a pilot circuit that includes:

- one modulating flow pilot, mounted outside of the filter tank in a stainless steel auxiliary reservoir connected to the tank by means of a 3 inch stainless steel pipe.
- one modulating stem regulator assembly mounted on the main angle valve, which maintains the opening degree according to the position of the flow pilot valve, given by the filter tank level.
- two solenold valves which can be deenergized individually to close or open the main valve completely; in normal modulating operation, both solenold valves are energized.
- one safety solenold valve, that closes tightly the main angle valve when there is a power failure. This modulating float valve provides an accurate control of the constant head loss by the assembly "filter-valve," which in its turn insures a constant rate of flow through the filters.

Operating and cost data (including data on efficiency, results, etc.):

The plant has been working since 1984 with no problems.

The cost of each unit complete with regulating and operation valves, is approximately 30 millions of liras.

Results achieved are excellent from all points of view. The plant consists of 10 units.

Place(s) of installation/application (including dates):

Water Treatment Plant by A.M.G.A. in Ravenna

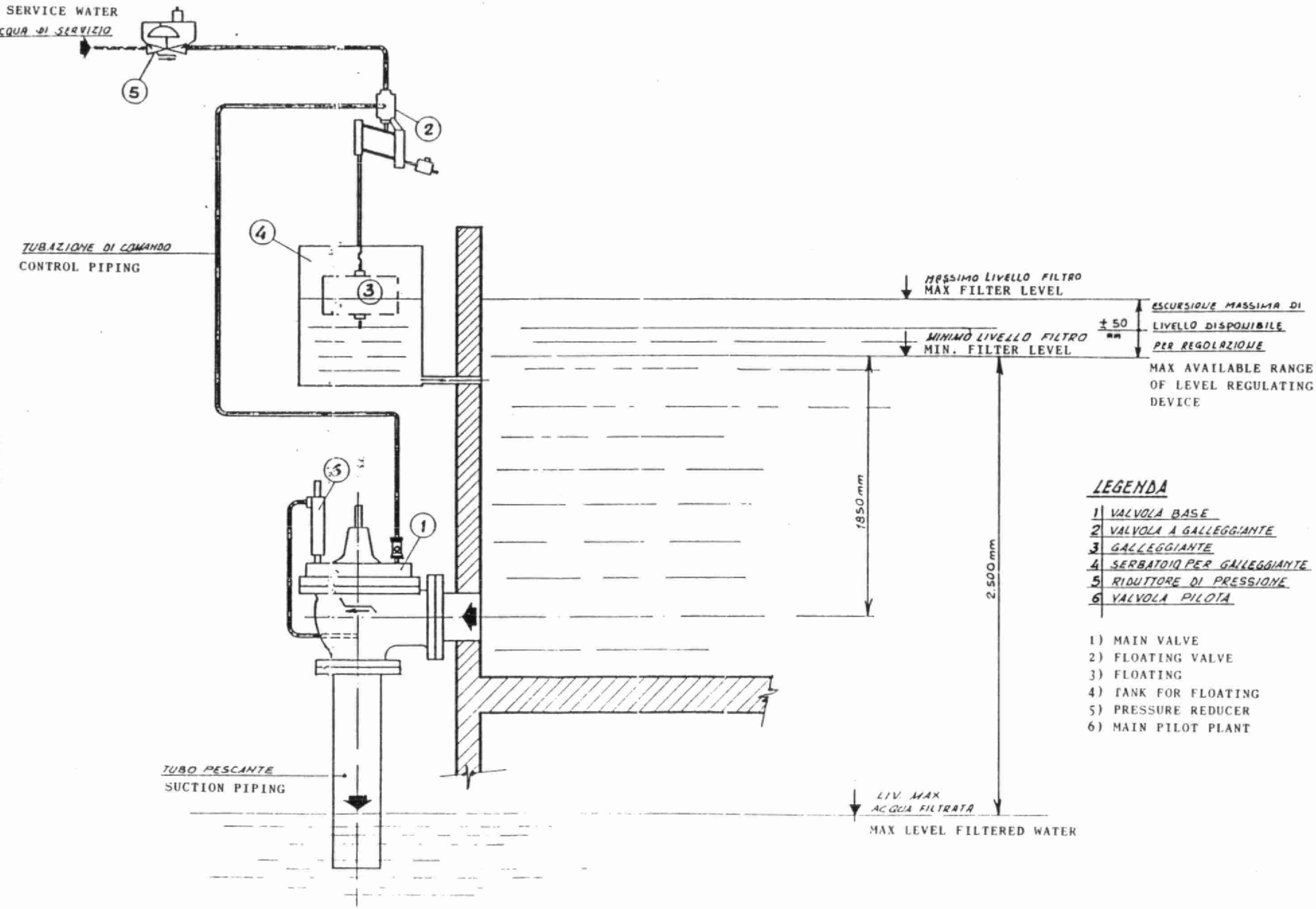
Patent staus, if applicable:

No patent.

Other information (e.g., funding source, cooperating agencies, etc.):

See display material to be available at the conference.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.


SERVICE WATER
ACQUA DI SERVIZIO
5
2
4
3
TUBAZIONE DI COMANDO
CONTROL PIPING
6
1
MASSIMO LIVELLO FILTRO
MAX FILTER LEVEL
MINIMO LIVELLO FILTRO
MIN. FILTER LEVEL
± 50 mm
ESCURSIONE MASSIMA DI
LIVELLO DISPONIBILE
PER REGOLAZIONE
MAX AVAILABLE RANGE
OF LEVEL REGULATING
DEVICE
1850 mm
2.500 mm
LEGENDA
1 VALVOLA BASE
2 VALVOLA A GALLEGGIANTE
3 GALLEGGIANTE
4 SERBATOIO PER GALLEGGIANTE
5 RIDUTTORE DI PRESSIONE
6 VALVOLA PILOTA
1) MAIN VALVE
2) FLOATING VALVE
3) FLOATING
4) TANK FOR FLOATING
5) PRESSURE REDUCER
6) MAIN PILOT PLANT
TUBO PESCANTE
SUCTION PIPING
LIV. MAX
ACQUA FILTRATA
MAX LEVEL FILTERED WATER

JAPAN

JAPAN

PROJECT DESCRIPTION

Project Title:

Studies on Biological Activated Carbon Filter Processes

Contact (name of person, organization, address, telephone):

Yoshinori KUROSAWA
Department of Sanitary Engineering, The Institute of Public Health,
Ministory of Health and Welfare
4-6-1, Shiroganedai, Minato-ku, Tokyo, 108 JAPAN
☎ 03-441-7111

Project Description (Please attach a schematic diagram if appropriate):

A seiries of pilot plant experiments were conducted to evalute the performance of biologically activated carbon(BAC) filters and sand filters in removal of turbidity and organic pollutants in raw water. The plant consisted of flocculator cell, setting cells, three columns each of BAC filters and sand filters, coagulant dosing equipment, and manometer apparatus.

Turbidity removal was satisfactory both in BAC filters and sand filters, although the latter did slightly better.

The BAC filters showed much better ammonium nitrogen removal rates than the sand filters, especially when the water temperature was low: and, when water temperature was falling, BAC filters maintained satisfactory removal rates whereas the latter lost removal function at the temperature of 10 degrees C.

The BAC filters demostrated the ablity to remove pottasium permanganate value(PV) from the start of operation while it took some 30 days of continuous run before the sand filters acquire removal capability. After such time, the rate of PV removal was at 60 to 70 % with the BAC filters and 30 to 60 % with the latter.

The THMFP and TOXFP removal rates by the BAC filters was almost 100 % at the beginning and reduced to about 50 % in about 70 days. Those by the sand filters was 10 to 15 % throughout the study period. Although the removal rates by the BAC filters declined gradually, even after 180 days, the rates of removal of THMFP and TOXFP were still at the level of 40 % and 50 % respectively: the regeneration property of the BAC filters was thus demostrated.

Operating and cost data (including data on efficiency, results, etc.):

Place(s) of installation/application (including dates):

Department of Sanitary Engineering, The Institute of Public Health, Ministry of Health and Welfare

20th June, 1983 started.

Patent staus, if applicable:

None

Other information (e.g., funding source, cooperating agencies, etc.):

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

PROJECT DESCRIPTION

Project Title:

Reduction of THM and Musty Odor by Ozonation and Granular Activated Carbon Treatment with Pilot Plant and Demostration Plant.

Contact (name of person, organization, address, telephone):

Hisahiko KIMURA
Osaka Municipal Waterworks Bureau
6-28, Minami-ohgimachi, Kita-ku, Osaka, 530 JAPAN
☎ 06-363-7300

Project Description (Please attach a schematic diagram if appropriate):

Osaka Municipal Waterworks Bureau established the first pilot plant($60 m^3/d$), combining various treatment processes such as GAC filtration and ozonation. Experiments with the pilot plant had been carried out for five years to find out useful means for the reduction of THM and musty odor in tap water.

As good results were obtained through the pilot plant studies, new demostration plant was established to study the condition for operation and maintenance, and to obtain the full-scale design criteria.

The capacity of the demostration plant is $2{,}000\ m^3/d$. It consists of two series, composed of rapid sand filters, ozonation basins, GAC filters and chlorination equipments, which are to receive settled water and to treat it at the rate of $1{,}000\ m^3/day$ each.

Experiments with the demostration plant have been carried out since April, 1986.

Operating and cost data (including data on efficiency, results, etc.):

It was confirmed that the process of ozonation followed by GAC filtration without chlorination, namely the biological GAC filtration, is capable of removing nearly all of the musty odor substances and reducing the THM precursors by 75 %.

Total cost of ozonation and GAC are estimated to be about 20 US cents/m^3.

Place(s) of installation/application (including dates):

The pilot plant was constructed at the site of Kunijima Water Purification Plant.
The demostration plants was constructed at the same site in March, 1986.

Patent staus, if applicable:

Not applied for patent.

Other information (e.g., funding source, cooperating agencies, etc.):

Funding source: Ourselves.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

PROJECT DESCRIPTION

Project Title:

Formaldehyde as a Key Index during Ozone Treatment
—Investigation on the behavior of formaldehyde and the precursor during ozonation—

Contact (name of person, organization, address, telephone):

Harumi YAMADA and Saburo MATSUI
Laboratory for Control of Envrionmental Micropollutants
Faculty of Engineering, Kyoto University
Yumihama, Ohtsu, 520 JAPAN
☎ 0775-24-6640

Project Description (Please attach a schematic diagram if appropriate):

Since halogenated organic compounds have been detected in drinking water, great interest has been directed toward the identification of the products of chemical oxidation processes. In order to get water treatment processes which provide safe and delicious tap water, it is necessary to have knowledge of the intermediate and end products formed during ozonation.

It is generally known that ozonation for a short or sufficient long period is effective in reducing mutagenicity, but incomplete ozonation creates compounds which show more mutagenicity than the original.

It is necessary to investigate the characteristics of intermediates.

Carbonyl compounds are formed from not only ozonation, but also during hydrolysis after ozonation. Glyoxal and metholglyoxal decompose during heating. Formaldehyde is mutagenic, not easily volatile and does not easily decompose during heating, it is clear that the existence of formaldeyde and its precursors at the initial stage of ozonation can not be disregarded. But, formaldehyde is decomposed by ozone.

Thus it is the key target of this project to investigate the relationship among (A) the amounts of formaldeyde and the precursor, (B) the other significant by-products and (C) ozone treatment conditions.

Operating and cost data (including data on efficiency, results, etc.):

Carbonyl Compounds and the precursors of carbonyl compounds which decompose to low molecular carbonyl compounds such as formaldehyde exist in ozonated waters. Their behaviors depend on water quality and ozone treatment conditions.

We have already developed the sensitive analysis method of carbonyl compounds by using o-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine(PFBOA) derivant.

We need to buy a gas chromatograph with ECD and cappilary column to investigate unknown compounds.

Total costs: US$ 30,000,(Gas Chromatograph「Shimazu GC-14APEsc」 $14,000, Labor cost $9,000 and Miscellaneous cost $7,000)
Project period: 2 years

Place(s) of installation/application (including dates):

The work is being done at Laboratory for Control Environmental Micropollutants, Faculty of Engineering, Kyoto University

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

Cooperating agency: Water Examination Laboratory of
Osaka Waterworks Bureau
(Demostration plant of ozonation and GAC treatment)

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

PROJECT DESCRIPTION

Project Title:

Detection and Evaluation of The DNA Damaging Potential of Mutagens in The Chlorinated and Ozonated Waters by The Bacillus Subtilis Rec-assay

Contact (name of person, organization, address, telephone):

Saburo MATSUI and Harumi YAMADA
Laboratory for Control of Environmental Micro pollutants
Faculty of Engineering, Kyoto University
Yumihama, Ohtsu, 520 JAPAN
☎ 0775-24-6640

Project Description (Please attach a schematic diagram if appropriate):

In order to detect and evalute the risk of mutagens and carcinogens in chlorinated and ozonated tap waters, it is a crucial matter for the water industry to develop a scientifically reasonable and technologically practical method to meet the problem.

The Ames method to detect mutagens is a most popular test method employed in the field of environmental mutagens. However, this method has many limitations such as no detection of THM as well as many other chlorinated organic substances resulted in poor correlation with carcinogenecity of those chlorinated organic substances.

We have developed the Bacillus subtilis liquid/microsome rec-assay system for detection of DNA damaging potential of substances in waters.

By this method, we succeeded in the detection of DNA damaging potential of THM as well as other many chlorinated organics. Many aldehydes of ozonated products also indicated DNA damaging potential by this method. Application of this method to polluted waters such as river waters, municipal waste-waters, nightsoil treatment plant waters all indicated occurence of DNA damaging substances in those samples. However, in order to apply this method for the real tap water samples, it is necessary to improve this method in several aspects including the development of stable pretreatment for concentration of sample waters and analysis of the result in terms of the risk assessment with other information of water samples etc.. The B. subtilis rec-assay is not a difficult technique to practice in the routine works. Information of this method covers the weak point of the information by the Ames method.

Operating and cost data (including data on efficiency, results, etc.):

We need to improve this method by application to many real samples of tap waters which are produced by chlorination and ozonation with activated carbon process. The project cost consists of labour-fee US$ 10,000, purchase of instruments and glasswares of sample concentration US$ 10,000 and micellanous items including chemicals US$ 10,000.
The total cost US$ 30,000 for 2 years.

Place(s) of installation/application (including dates):

Laboratory for Control of Environmental Micropollutants
Faculty of Engineering, Kyoto University
Ohtsu City, Japan

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

Cooperating agency: Water Examination Laboratory of Osaka Water Works Bureau
(Demostration plant of Ozonation and GAC treatment)

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

EMERGING WATER SUPPLY TECHNOLOGY

AWWARF Code #: JP-05

PROJECT DESCRIPTION

Project Title:

Treatment Study of the Yodo River Water using Submerged Bioreactor combined with GAC filtration and Ozonation

Contact (name of person, organization, address, telephone):

Masami YAMAMOTO
Water Supply Division, Department of Waterworks,
Osaka Prefectural Government
2-22, Tanimachi, Higashi-ku, Osaka, 540 JAPAN
☎ 06-941-0351

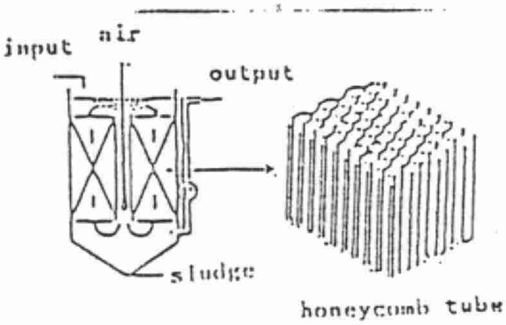
Project Description (Please attach a schematic diagram if appropriate):

Raw water, the Yodo River surface water, Japan, has deteriorated in recent years. Therefore, the finished water made with such raw water is not delicious and may contains many organic substances.

The purpose in the study was to comprehend effects of the eliminating of an ammonia-nitrogen, musty ordor substances, TTHM precursor and other organic pollutants by the advanced purification technology. In the study, we used a pilot plant having bellow processes.

Raw—Biological treatment—Coagulation—Sedimentation—
Rapid sand filtration—Ozonation—GAC filtration—
Postchlorination—Finished water

Biological treatment is carried out by the Submerged Bioreactor(SBR) shown as the figure. Polypropylene tubes like a honeycomb, which is called Honeycomb Tube, is installed in the SBR basin, and air diffuser is set under the Honeycomb Tube. Raw water led in the SBR basin is recycled by aeration. During that time, it is purified by micro organism adhered on the inside wall of the honeycomb tube.



Operating and cost data (including data on efficiency, results, etc.):

The pilot plant test was carried out at flow rates of 33~45 m³/day. Other conditions are summarized bellow.

SBR basin: Recycle velocity 3m/min., Load of water volume 0.13~0.17 m³/m²/day, Retention time 100 min.

GAC column: LV 15m/hr. down flow, Height of GAC bed 1.4 m

Ozonation column: Ozone dosage is 1~3 g/m³

The results obtained in the study are shown bellow.

- Ammonia nitrogen were eliminated by 75 % in winter and by 85 % in other seasons by the SBR only.
- Musty odor substances such as geosmin, 2-methl-isoborneol were eliminated by 50~80 % by the SBR only.

Place(s) of installation/application (including dates):

The study was conducted at Niwakubo Purification Plant which intakes surface water of the Yodo River, which flow through Osaka Prefecture, from 1985 to 1987.

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

Cost of the Study: ¥ 33,500,000

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

EMERGING WATER SUPPLY TECHNOLOGY AWWARF Code #: JP-06

PROJECT DESCRIPTION

Project Title:

Biotreatment of Lake Water

Contact (name of person, organization, address, telephone):

Yuichi FUCHU and Shigeo YASUTAKE
EBARA Resarch Co.,Ltd.
4-2-1, Honfugisawa, Fujisawa, 251 JAPAN
☎ 0466-81-1121

Project Description (Please attach a schematic diagram if appropriate):

In recent years, we see a significant number of resarch projects carried out on biotreatment of water for supply system. This trend is a conseque-nce of a growing demand for technological improvement in watertreatment plant processes, particularly for pollutant control to ensure a supply of hygienically pure potable water to the ever-incresing urban and city population.

The authors of this paper have conducted studies on the submerged filter used for contact aeration and the biological aerated filter(BAF)used for biological filtration, for objecting to clarify some biotreatment chara-cteristics in treating potable water.Experiments utilizing a pilot plant were conducted over a period of approximately one year.

This paper discusses data obtained throughout four seasons which include: reduction features of odor, ammonia and THM formation potential, and the purification effects in submerged filter.

The dimensions of the pilot plant are shown on Table 1.

Table 1 Dimension of Pilot plant

Item \ Method		Submerged Filter		BAF
		Type I	Type II	
Size		$0.5m^W \times 1.7m^L \times 2.3m^H$	$0.5m^W \times 1.7m^L \times 2.3m^H$	ϕ $0.4m \times 5m^H$
Media Volume		$1.1m^3$	$1.1m^3$	$0.25m^3$
Media	Kind	Honeycomb tube	Honeycomb tube	Anthracite
	Opening or Particle size	Opening 8mm	Opening 8mm	Particle 3~6 mm
	Specific surface	272 m^2/m^3	272 m^2/m^3	1100m^2/m^3

Operating and cost data (including data on efficiency, results, etc.):

As for removal of 2-MIB, GMS and NH_4-N, a trend exists where there is a dependency on the loading rate per surface area unit of adhereded biological film. As for the THM formation potential, there was no trend of dependency on the loading rate per surface area and the removal rate was found to be 0~30 %.

After conducting a feasibility study centered on the biotreatment of 100,000 m^3/day, it was found that there was no difference in the initial cost according to by method(approx. 2~2.5 billion yen). As for the running cost of aeration, the cost of running the submerged filters came to 0.9 yen/m^3 and that for running the BAF came to 0.4 yen/m^3.

Place(s) of installation/application (including dates):

Location: Kasumigaura, Ibaragi Prefecture
Period: from Dec. 1986 to Nov. 1987

Patent staus, if applicable:

Title: Biological Filter
JP Utility Model Reg. No. 1656076
Inventor: Yuichi FUCHO, Yoshiro HAYASHI
Assignee: EBARA-INFILCO Co., Ltd. Tokyo, JAPAN

Other information (e.g., funding source, cooperating agencies, etc.):

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

EMERGING WATER SUPPLY TECHNOLOGY AWWARF Code #: JP-07

PROJECT DESCRIPTION

Project Title:

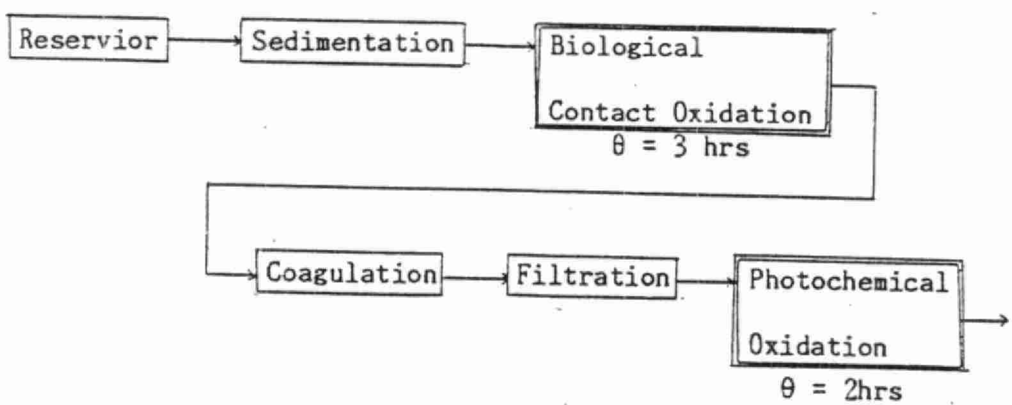
Purification of Polluted Water Resource for Supplying Industrial Process Water by Biological and Photo-chemical Treatment

Contact (name of person, organization, address, telephone):

Michio HIROSE
TORAY Engineering Co.,Ltd.
3-4-18(Mitsui №2 Bld.), Nakanoshima, Kita-ku, Osaka, 530 JAPAN
☎ 06-448-5151
Gennosuke INOUE
Water Re-Use Promotion Center
2-3-4, Akasaka, Minato-ku, Tokyo, 103 JAPAN ☎ 03-583-9431

Project Description (Please attach a schematic diagram if appropriate):

The Biological Contact Oxidation is used vertical net layer such as fish-net and it does biological oxidation in basin. The Photochemical oxidation is used artificial light such as ultraviolet rays and it does oxidation. This method is combined biological contact oxidation and photochemical oxidation case by case.



	Objectives of Treated Water Quality	Average Raw Water Quality: Summer	Average Raw Water Quality: Winter
CODMn	< 2.0 mg/ℓ	6	9
NH4-N	< 1.0mg/ℓ	2	5
SS	< 1.0mg/ℓ	-	-

Operating and cost data (including data on efficiency, results, etc.):

1. Case study(based on test operating data)--50,000 m³/day
   - -Initial cost: 1.7(Billion Yen)---Upgrading
     4.0(Billion Yen)---Newly construction
   - -Running cost: 1.1(Yen/m³)--------in Summer
     8.4(Yen/m³)--------in Winter

2. Adaptability testing
   Good adaptability for dyeing and electro-plating Process was confirmed.

Place(s) of installation/application (including dates):

Bench-scale test was done during 1982 and Pilot-scale plant was operated during 1983~1984 at Tamagawa Purification Plant, Tokyo Waterworks Bureau.

Patent staus, if applicable:

Title: Wastewater Treatment Appratus(Biochemical contact oxidation)
JP Patent No.1113575(1981-22598)

Title: Water Treatment Method and its Aprratus(Photochemical oxidation)
JP Patent No.1143715(1977-22598)

Other information (e.g., funding source, cooperating agencies, etc.):

This project was carried as one of the tasks of Water Re-Use Promotion Center and supported by Japanes Bicycle Promotion Association.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

EMERGING WATER SUPPLY TECHNOLOGY

AWWARF Code #: JP-08

PROJECT DESCRIPTION

Project Title:

Practical Application of A.I. in Optimum Water Supply System

Contact (name of person, organization, address, telephone):

Haruo ITOH and Masanori MORIMOTO
Water Treatment Dept. I, Technical Coordination Div.
Fuji Electric Co.,Ltd.
1-12-1, Yurakucho, Chiyoda-ku, Tokyo, 100 JAPAN
☎ 03-211-7111

Project Description (Please attach a schematic diagram if appropriate):

A mathematical programming method for an optimum water supply system is already being put to use.

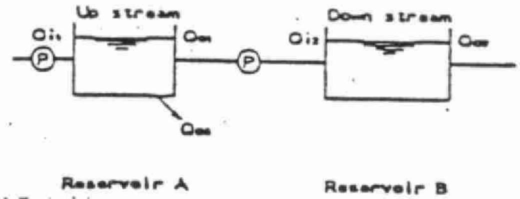
However, covering all variable factors that may occur on a large scale system, such as accidents, stoppage of equipment and expansion of facilities, is nearly impossible. On the other hand, the experienced operator covers all the variables of the complex water system operations manually in a satisfactory manner. Additionally, there are contradictory factors to the target function of the mathematical programming method and there is need to place importance on each of these individual factors but it has been not possible to clearly define them into one.

Therefore, a basic plan using the mathematical programming method and placement of the factors in order of importance was specified.

An operational system applying A.I. expert knowledge for handling operation under abnormal operational conditions such as accidents, was developed. In order to handle the water supply system for a large area, a partial system to be used as a prototype is being put into application. The configuration of the expert system is shown in the attached illustration.

Operating and cost data (including data on efficiency, results, etc.):

Power consumption of pumps for water reservoirs connected in series are shown in the diagram.



Item \ Case	Distribution form DP method + Knowledge base	Heap DP method	Water level control method
Power consumption (kwH/DAY)	16508.5 (98.3%)	16576.1 (98.7%)	16795.6 (100%)

Place(s) of installation/application (including dates):

Water supply control computation system at Kobe water supply system(1988)
Number of transmission tunnels : 11
Number of reservoirs : 90

Patent staus, if applicable:

None

Other information (e.g., funding source, cooperating agencies, etc.):

Joint-development organization, Kobe City Waterworks Bureau.
In the future, the pump and/or the control valve will be switched over from operator guidance to full automatic control.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

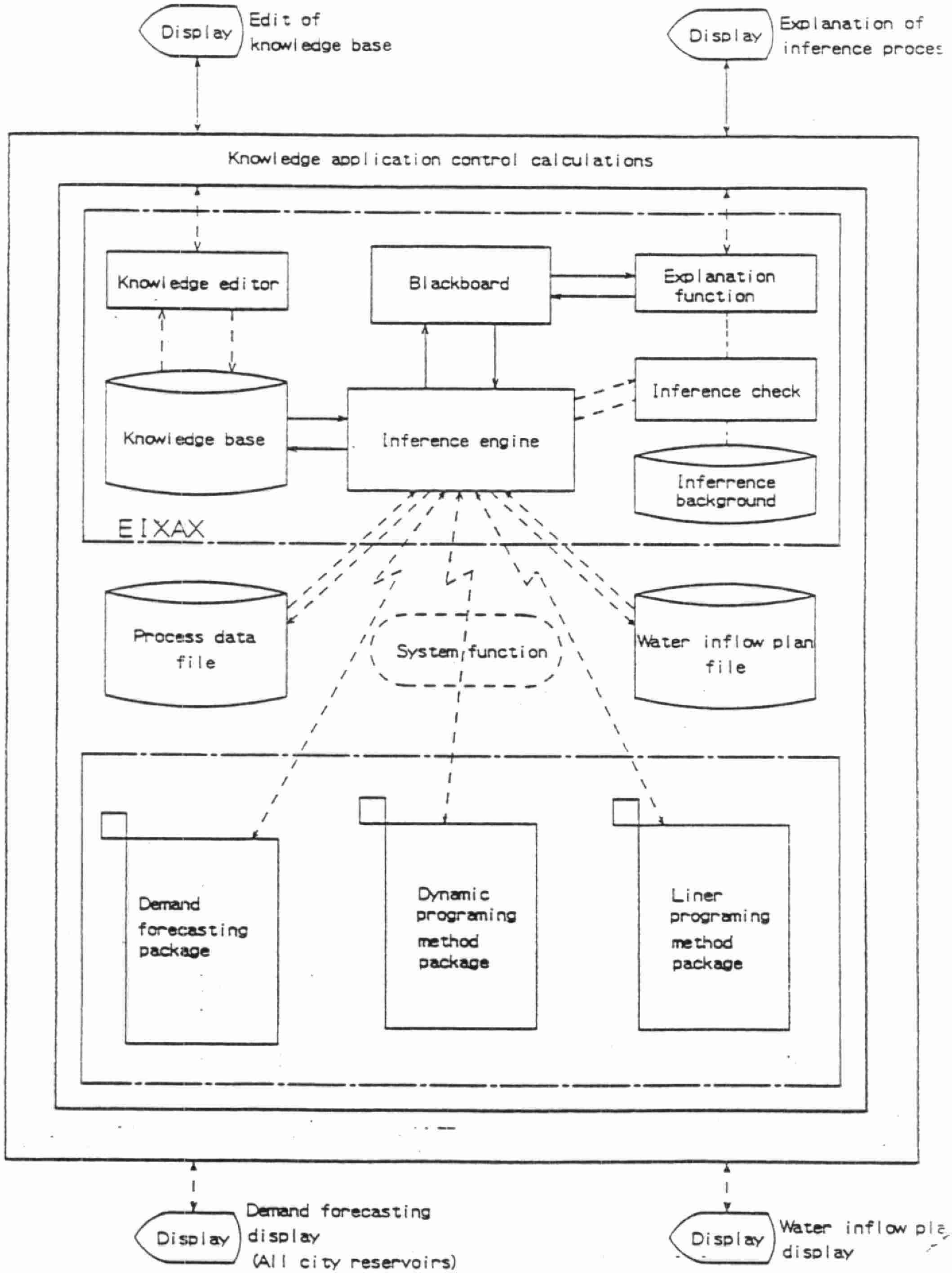


Figure 1 Water supply and distribution line network expert system

NETHERLANDS

THE NETHERLANDS

EMERGING WATER SUPPLY TECHNOLOGY AWWARF Code #: NE-01

PROJECT DESCRIPTION

Project Title:

Ultra violet (UV)disinfection of drinking water

Contact (name of person, organization, address, telephone):

Dr. J.C. Kruithof,
KIWA N.V.
P.O. Box 1072
3430 BB RIJSWIJK
The Netherlands (Telephone) 03402 - 60 8 60

Project Description (Please attach a schematic diagram if appropriate):

For post disinfection purposes either chlorinegas or sodium hypochlorite is added to the water. This addition causes a rise in the concentration of THM's and high molecular organohalogens. Besides a rise of the mutagenicity in the Ames test is noticed.

For some water types with a low content of biodegradable compounds there is no need to maintain a post chlorination. However, especially after GAC-filtration as the final treatmentstep the colony counts in the finished water may be relatively high. UV-disinfection is investigated as an alternative post-disinfection step to reduce these colony counts.

Experiments on pilot plant scale showed that UV-disinfection produced drinking water which meets all the bacteriological standards. Therefore the project is continued at a full scale base. In these experiments the effect of UV-disinfection with low and medium pressure UV-burners is investigated. Knowledge is gained about:

- The disinfection properties of both systems
- The required UV-dosage
- Potential side effects
- Handling
- Costs

At this moment about one year full scale experience is available.

Operating and cost data (including data on efficiency, results, etc.):

Drinking water which meets all bacteriological requirements can be produced from GAC-filtrate with high colony counts with both UV-disinfectors. When necessary a more than 1000 fold reduction of PCA 22 °C can be achieved. The required UV-dosage proves to be about 12 mJ/cm².

To characterize the side effects the assimilable organic carbon (AOC) content and the mutagenicity in the Amestest have been determined. Both parameters are not increased by UV-disinfection. For that reason UV-disinfection does not cause regrowth in the distribution system and does not produce mutagenic compounds. The apparatus for UV-disinfection can be handled easily. The major drawback is the monitoring of the UV-dosage. The costs of the total UV-disinfection step (depreciation, maintenance, energy consumption) proves to be about fl 0,010 - f 0,015 per m³ of drinking water.

Place(s) of installation/application (including dates):

Waterworks of North West Brabant, treatment plant of Zevenbergen (1987).

Additional investigations:

Waterworks "De Alblasserwaard & Vijfheerenlanden" treatment plant of Hardinxveld (1983)

Municipal Waterworks Maastricht, treatment plant De Tombe (1985).

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

The research at Zevenbergen is funded by the Netherlands Waterworks Association (VEWIN) together with the Waterworks of Northe West Brabant. All other research is funded by VEWIN only.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

Removal of Nitrate by Slow Sulphur/Limestone Filtration

J. C. Schippers and **J. C. Kruithof**, *KIWA N.V., 2280 AB Rijswijk, The Netherlands*
F. G. Mulder, *Gelderland Eastern Water Supply Company, The Netherlands*
J. W. van Lieshout, *Water Laboratory of the Eastern Netherlands Waterworks, The Netherlands*

Abstract: Slow sulphur-limestone filtration aims to be a simple and reliable process for the removal of nitrate from groundwater. In this process nitrate is removed in an upflow filter containing sulphur and limestone with help of the bacterium *Thiobacillus denitrificans*. The filter operates at a rate of 0.25 m/h which implies that backwashing is not required.

Before the denitrification process starts the oxygen and nitrogen of the water is removed with a vacuum deaerator as these compounds disturb the process. After the denitrification the water is aerated and infiltrated in the soil, in order to remove bacteria, biodegradable matter and turbidity.

Recently a demonstration plant with a capacity of 35 m^3/h has been put in operation.

Elimination du nitrate avec la filtration lente au soufre-maerl

Résumé: La filtration lente au soufre-maerl est un procédé simple et fiable pour éliminer les nitrate des eaux souterraines. Dans ce procédé le nitrate est enlevé dans un filtre à courant ascendant composé d'un mélange de soufre et de calcaire par la bactérie *Thiobacillus dénitrificans*. Une lavage du filtre n'est pas necessaire, parce que la vitesse de filtration est 0,25 m/h.

Pour éviter une interférence dans le procédé l'oxygène et l'azote sont eliminés par un dégazeur à vide avant la dénitrification. Après la dénitrification l'eau est aerée et infiltrée dans le sol pour éliminer les bactéries, les elements biodegradables et la turbidité.

Les premiers essais pratiques ont commencé récemment avec une installation de démonstration d'une capacité de 35 m^3/h.

Introduction

At many groundwater catchment areas the nitrate concentration in the water is showing a definite increase. The Maximum Acceptable Concentration of 50 mg nitrate per litre laid down in the Dutch Drinking Water Act has already been reached at two such catchments areas.

The main cause of rising nitrate concentrations in the Netherlands is excessive use in agriculture of animal manure. Besides this, normal fertilizing with manure and artificial fertilizers, acid rain and leaking sewer systems also contribute to the nitrate problem.

It is anticipated that in the near future problems will arise in some 80 out of the total number of 250 groundwater catchment areas.

This problem is not confined to the Netherlands. Our neighbouring countries are also faced with rising nitrate contents in groundwater and surface water, while outside Europe the problem is just as serious. In fact, the steady rise of nitrate content in groundwater and surface water is now a threat to drinking water supply in more and more parts of the world and corrective measures are obviously needed as a matter of urgency. Any drastic restriction on the (excessive) fertilizing of agricultural land in the Netherlands is stoutly resisted by the farming sector. In the present social climate it is unrealistic to expect any worthwhile limitation on overfertilizing in the short term.

Moreover, any drastic reduction in overfertilizing would take several years to lower the nitrate content in the extracted groundwater. The fact is that by the time it reaches the extraction wells, groundwater has generally had an average underground residence time of several years. This situation forces waterworks to consider ways and means for assuring the quality of their drinking water in the immediate future. The possible options are:

— to impose restrictions on overfertilizing in protecting zones of the groundwater catchment area;
— to abstract water from another groundwater catchment area or to mix water having a high nitrate content with nitrate-free water that would have to be brought from elsewhere;
— to produce drinking water from surface water.

However, these measures are feasible in only a few situations. Consequently, the waterworks have in many situations no alternative but to remove the nitrate from the drinking water.

Processes into the removal of nitrate

A wide range of physico-chemical and biological processes are currently being developed for the removal of nitrate from drinking water. Biological denitrification processes specifically remove nitrate from drinking water while their physico-chemical counterparts are less specific and may therefore also remove other inorganic substances.

Physico-chemical processes

Ion exchange and reverse osmosis are proven techniques for removing inorganic salts. The most serious drawback to these techniques is the production of effluents in the form of brine whose disposal is often difficult so that these techniques are less commonly used. Evaporating the water from the brine to leave the salts in solid form is too costly and complicated a process to be worthwhile.[1]

Biological purification of the regenerant solution used in ion exchange with say methanol promises an appreciable reduction in the amount of brine that has to be discharged.[2] Still, this method has the disadvantage of being rather complicated.

A combination of cation and anion exchange with the dual aim of softening and nitrate removal enables regeneration to be carried out with carbon dioxide. This too can minimize the quantity of brine produced.[3]

However, anion exchange involves the risk of quaternary ammonium compounds entering the treated water. Since these compounds are suspect from the standpoint of public health, the problem clearly demands caution and attention.

Biological denitrification

Nitrate can be converted to nitrogen by bacteria in anaerobic conditions. Heterotrophic bacteria convert nitrate by making use of organic substances such as methanol, ethanol and acetic acid. The denitrification with methanol proceeds according to the following reaction:

$$5\,CH_3OH + 6\,NO_3^- \rightarrow 5\,HCO_3^- + OH^- + 7\,H_2O + 3\,N_2.$$

Autotrophic bacteria make use of inorganic substances like hydrogen and sulphur as their energy source. Denitrification with hydrogen follows the reaction:

$$5\,H_2 + 2\,H^+ + 2\,NO_3^- \rightarrow N_2 + 6\,H_2O.$$

In both processes biomass is produced as well as inorganic substances.

Autotrophic and heterotrophic bacteria both need phosphate as an essential element for their growth. In laboratory conditions the denitrification processes present no problems but little experience has yet been gained on their practical application. There are at present in Europa only a few demonstration installations where such practical experience is being obtained. Various process versions are being tested in these installations, namely:

— fluidized bed (with methanol)
— fixed bed with ethanol and/or acetic acid downflow
— fixed bed with ethanol upflow
— floating bed with ethanol upflow
— profiled lamellae (with hydrogen).

The aim of these process versions is to create within a limited space a large suface for adherence of bacteria. At the same time the flow conditions in the system are adjusted such that the mass transfer shall take place sufficiently fast. These techniques have various drawbacks, namely:

(a) they are complicated compared to the processes generally employed in groundwater pumping stations, e.g. aeration and rapid filtration;
(b) the denitrified water generally contains biodegradable matter in the form of biomass, thus demanding intensive post-treatment.

An alternative to denitrification in a treatment plant is the removal of nitrate in situ, ie. in the soil. This process is in principle free from the abovementioned drawbacks. It is also comparatively cheap. Full-scale investigations carried out by the Gelderland Eastern Water Supply Company and others have shown that the injection well employed soon becomes clogged by bacterial growth.[4] This means that the technique will only be technically possible once the clogging problem has been solved. Furthermore, with soil protection in mind, the government views the use of this technique with a rather jaundiced eye.

Reviewing the available techniques for removal of nitrate, it is apparent that none have yet proved simple, reliable and cheap in practical application over a reasonably long period of time.

Choice of process and location of investigation

Small groundwater pumping stations are mostly unmanned, generally rather basic and often of limited capacity. For removing nitrate from the groundwater handled by these pumping stations it is therefore clearly preferable to use simple processes requiring little supervision. Consequently, process selection and conduct of experiments is always geared to the need for the process to be suitable for practical application at such pumping stations.

After thorough evaluation of possible processes for the removal of nitrate from groundwater, it was concluded that biological denitrification in a fixed bed with sulphur and limestone is in principle simple, reliable and reasonably cheap.[5]

The version chosen for this process is comparable to slow sand filtration. A further requirement was that a simple secondary treatment must suffice to remove biomass from the denitrified water.

As sulphate is formed as a sideproduct the use of the sulphur/limestone process is restricted to pumping stations where the sulphate content of the raw groundwater is low enough for the sulphate standard not to be exceeded after denitrification. The Dr J. H. van Heek pumping station belonging to the Gelderland Eastern Water Supply Company meets this requirement and it was therefore decided that this should be the site for a preliminary investigation into the feasibility of the process.

The sulphur/limestone process

Principle

Autotrophic bacteria like *Thiobacillus denitrificans* are capable of converting nitrate to nitrogen in the presence of elementary sulphur according to the following reaction:

$$5\,S + 6\,NO_3^- + 2\,H_2O \rightarrow 3\,N_2 + 5\,SO_4^{2-} + 4\,H^+.$$

Beside the inorganic substances nitrogen, sulphate and hydrogen ions, biomass is also formed.

$$55\,S + 50\,NO_3^- + 38\,H_2O + 20\,CO_2 + 4\,NH_4^+ \rightarrow$$

$$4\,C_5H_7O_2N + 25\,N_2 + 55\,SO_4^{2-} + 64\,H^+.$$

Denitrification is accompanied by the formation of hydrogen ions which lowers the pH value. However, for optimal bacterial action the pH should preferably be between 6.4 and 6.8 and neutralization is therefore necessary.

For this purpose limestone granules are added to the sulphur to maintain the pH level during the process. A lot of work in this field has been done by Martin and co-workers[6,7] working with a fixed bed of limestone and sulphur. Laboratory scale experiments performed at a filtration rate of 1 m/h yielded very promising results but practical application calls for further investigations.

Pilot plant experiments (phase 1)

The following preconditions were laid down for the pilot plant experiments:

— Supersaturation with nitrogen, with consequent formation of nitrogen bubbles in the bed, should be countered.
— The loss of active biomass through backwashing of the sulphur/limestone bed should be avoided.
— The biomass and other biodegradable matter present in the denitrified water should be removable by infiltration into the soil.

In this series of pilot plant experiments nitrogen supersaturation was countered by providing a positive head of 50 kPa. At a later stage supersaturation was prevented by deaerating the untreated groundwater.

Upflow filtration is applied in order to make it easier for the nitrogen bubbles to escape assuming that this formation of these bubbles cannot be completely prevented.

Another no less important argument in favour of upflow filtration is to prevent the introduction of nitrogen and oxygen into the water.

The filtration rate selected was 0.5m/h (the rate used in slow sand filters). This decision was conditioned by the fact that Martin's results had been not entirely satisfactory at a rate of 1 m/h at which regular backwashing of the filter bed also appears to have been important.

A combination of a lower filtration rate, omission of backwashing plus removal of nitrogen and oxygen by deaeration should well ensure efficient operation. The criterion for this is 90% nitrate removal over a period of at least 1 year and preferably 2 years without unacceptable clogging of the filter.

The experiments were carried out in filters of diameter 0.30 m filled with sulphur and limestone granules (ratio 1:1, depth 1.50 m) at a filtration rate of 0.5 m/h. The water was introduced

from below after addition to it of 0.2 mg/l PO_4^{3-}. A parallel experiment was also carried out with no phosphate added.

The clogging potential of the denitrified water was investigated in a preliminary experiment with an apparatus for the measurement of the artificial recharge filtration index.

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The effect of slow sulphur/limestone filtration on several essential parameters is shown in Table 1.

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In view of the encouraging results obtained in the preliminary experiments, it was decided:

(a) To continue the experiments with an extended pilot plant under adjusted process conditions.

(b) To carry out further investigations into the clogging potential of the denitrified water from the pilot plant.

(c) To design a demonstration plant with a capacity of 35 m^3/h whose effluent would be infiltrated into the soil.

After the pilot plant had been extended by addition of a vacuum deaerator, the treatment process was as follows:

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Pilot plant experiments (phase 2)

Vacuum deaerator. The groundwater for processing is deaerated for removal of nitrogen and oxygen. Removal of nitrogen is necessary in order to prevent the water becoming supersaturated with the nitrogen generated during the denitrification process with formation of gas bubbles that will surround the sulphur granules. This impedes mass transfer to and from the sulphur granules and greatly reduces the denitrification efficiency. In addition, nitrogen bubbles cause channeling in the filter bed.

The concurrent removal of oxygen also has a good effect in that the oxygen in the sulphur/limestone bed no longer has first to be removed by bacteria. In other words, were it not for degassing, part of the sulphur/limestone bed would not be available for the denitrification process. Another advantage of oxygen removal is to minimize the formation of sulphate.

Slow sulphur/limestone filtration. After deaeration, the water is introduced from below into a filter filled with sulphur (2–6 mm) and limestone (2–5 mm) in a 1:1 volume ratio. The depth of the sulphur/limestone bed was reduced from 1.50 to 0.75 m. If the nitrate removal decreases, the filter bed can be increased to 1.5 m.

Should breakthrough occur again at a bad depth of 1.5 m the filter material in a full-scale plant would have to be cleared of biomass.

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Some of the effluent from the slow sulphur/limestone filter is passed to an installation with four small test filters. In these filters infiltration into the soil is simulated at various filtration rates. By this means an idea can be quickly obtained of the extent to which the soil may become clogged during infiltration.

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In the pilot plant investigation it appears that the nitrogen content can be reduced to 1–2 mg/l and the oxygen to 0.5–1 mg/l with the vacuum deaerator. By way of comparison a parallel experiment was carried out in a second slow sulphur/limestone filter supplied with undegassed water. After 50 days this filter no longer fully removed the nitrate. As against this, the filter supplied with degassed water still removes the nitrate 100% after 200 days, and this with hardly any increase in filter head loss.

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The results obtained on the pilot plant gave such a promising outlook for full-scale application of the process that it was decided to build a demonstration plant with a capacity of 35 m^3/h. This plant comprises:

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- Cascade
- Infiltration pond

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Summary and conclusions

(a) Investigations with a pilot plant have shown that the sulphur/limestone process combined with vacuum deaeration and infiltration of the denitrified water can offer a simple and reliable technique for the removal of nitrate from groundwater. However, the application of this technique is confined to situations where groundwater with a low sulphate content is present and infiltration is possible.

(b) The demonstration installation based on the sulphur/limestone process operated during more than four months quite satisfactorily. The process will have to show within the next 2 years whether it does indeed live up to expectation in practice.

Acknowledgements

The project described is being carried out at the request of the Netherlands Waterworks Association supported by a grant from the Department of Drinking and Industrial Water Supply of the Ministry of Housing, Physical Planning and Environment.

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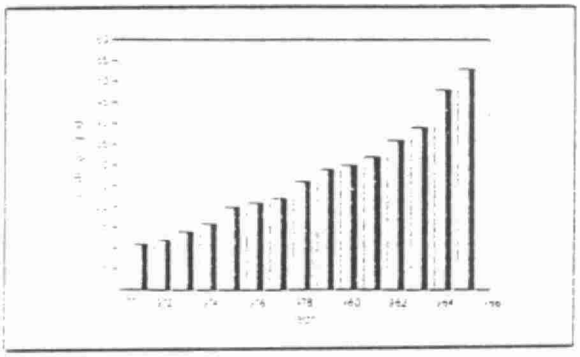

Fig. 1. Nitrate concentration in the abstracted groundwater in the Montferland over the period 1970–1986

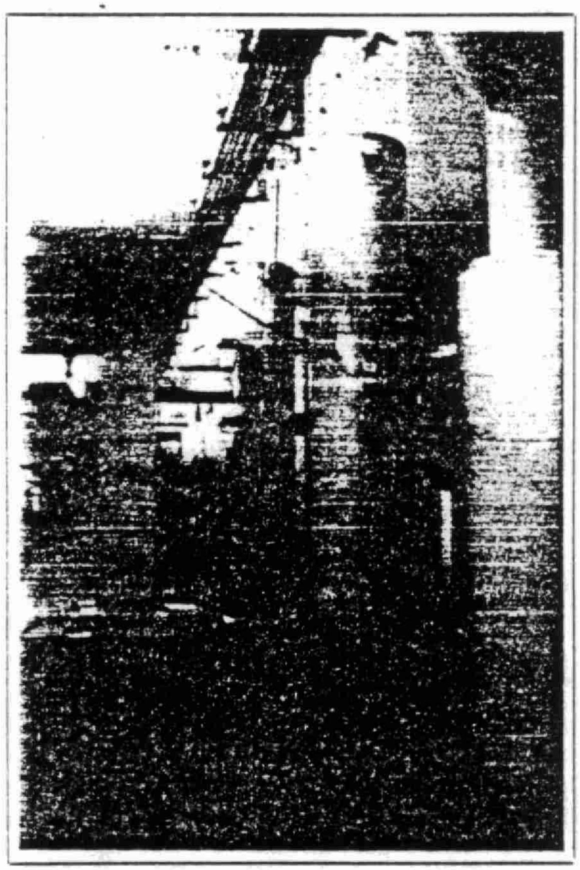

Fig. 2. The pilot plant for removing nitrate from groundwater with sulphur and limestone

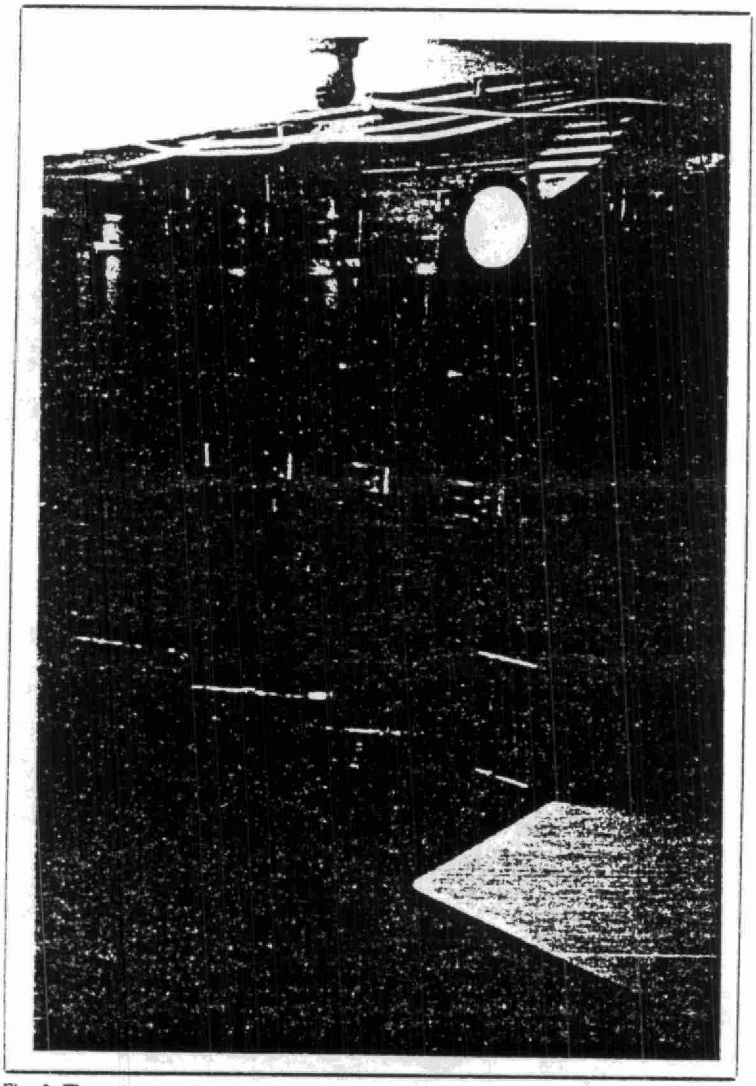

Fig. 3. The apparatus for the measurement of the artificial recharge filtration index of the denitrified groundwater

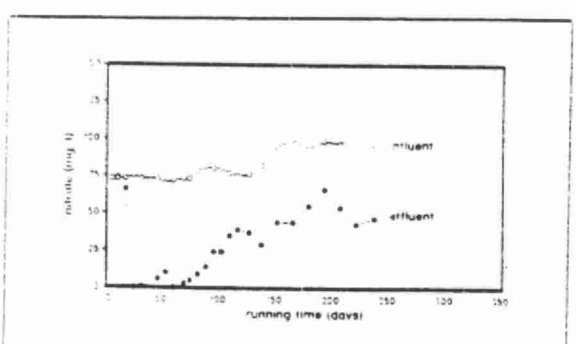

Fig. 4. The effect of slow sulphur/limestone filtration without prior vacuum deaeration

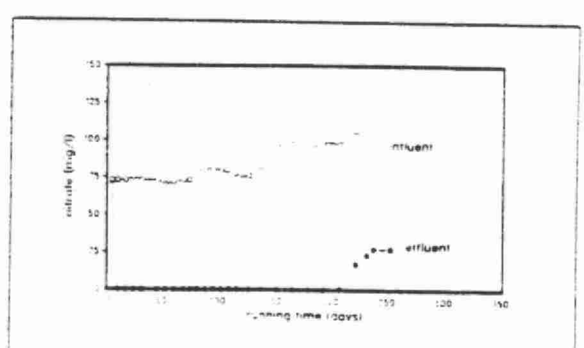

Fig. 5. The effect of slow sulphur/limestone filtration after prior vacuum deaeration

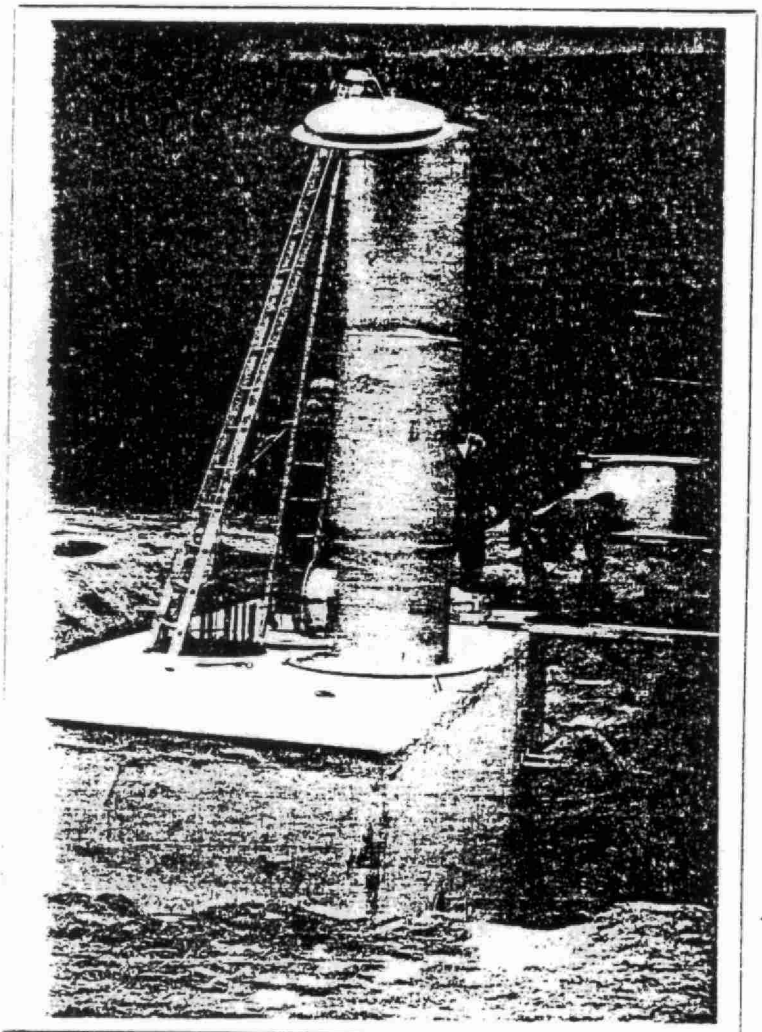

Fig. 6. The vacuum ... water due to be denitrified

Fig. 7. The slow sulphur ...

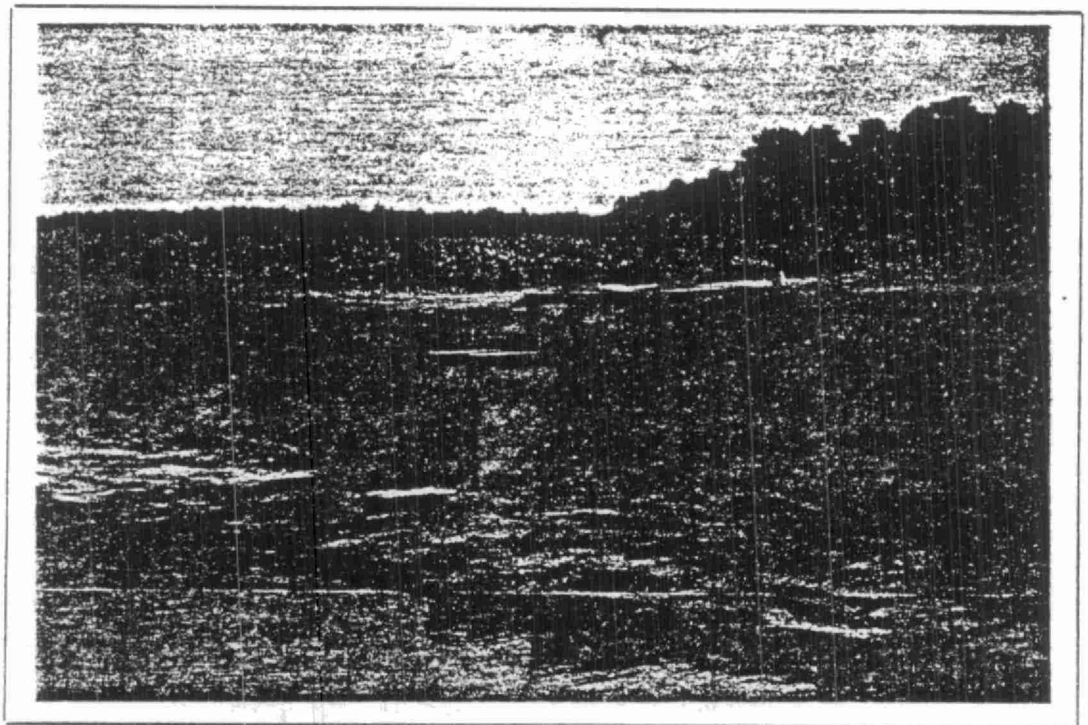

Fig. 8. The infiltration pond with cascade

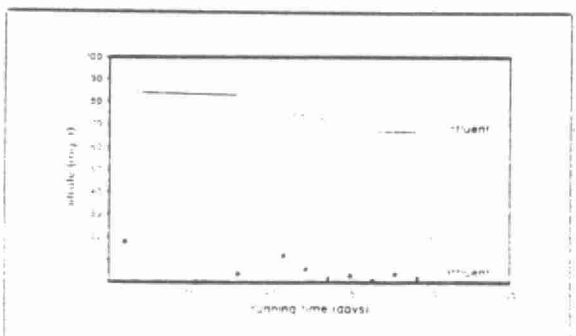

Fig. 9. The effect of the slow sulphur/limestone process on demonstration scale during the first three months of operation

NE 2

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F. G. Mulder, *Gelderland Eastern Water Supply Company, The Netherlands*
J. W. van Lieshout, *Water Laboratory of the Eastern Netherlands Waterworks, The Netherlands*

Abstract: Slow sulphur-limestone filtration aims to be a simple and reliable process for the removal of nitrate from groundwater. In this process nitrate is removed in an upflow filter containing sulphur and limestone with help of the bacterium *Thiobacillus denitrificans*. The filter operates at a rate of 0.25 m/h which implies that backwashing is not required.

Before the denitrification process starts the oxygen and nitrogen of the water is removed with a vacuum deaerator as these compounds disturb the process. After the denitrification the water is aerated and infiltrated in the soil, in order to remove bacteria, biodegradable matter and turbidity.

Recently a demonstration plant with a capacity of 35 m^3/h has been put in operation.

Elimination du nitrate avec la filtration lente au soufre-maerl

Résumé: La filtration lente au soufre-maerl est un procédé simple et fiable pour éliminer les nitrate des eaux souterraines. Dans ce procédé le nitrate est enlevé dans un filtre à courant ascendant composé d'un mélange de soufre et de calcaire par la bactérie *Thiobacillus dénitrificans*. Une lavage du filtre n'est pas necessaire, parce que la vitesse de filtration est 0,25 m/h.

Pour éviter une interférence dans le procédé l'oxygène et l'azote sont eliminés par un dégazeur à vide avant la dénitrification. Après la dénitrification l'eau est aérée et infiltrée dans le sol pour éliminer les bactéries, les élements biodegradables et la turbidité.

Les premiers essais pratiques ont commencé récemment avec une installation de démonstration d'une capacité de 35 m^3/h.

Introduction

At many groundwater catchment areas the nitrate concentration in the water is showing a definite increase. The Maximum Acceptable Concentration of 50 mg nitrate per litre laid down in the Dutch Drinking Water Act has already been reached at two such catchments areas.

The main cause of rising nitrate concentrations in the Netherlands is excessive use in agriculture of animal manure. Besides this, normal fertilizing with manure and artificial fertilizers, acid rain and leaking sewer systems also contribute to the nitrate problem.

It is anticipated that in the near future problems will arise in some 80 out of the total number of 250 groundwater catchment areas.

This problem is not confined to the Netherlands. Our neighbouring countries are also faced with rising nitrate contents in groundwater and surface water, while outside Europe the problem is just as serious. In fact, the steady rise of nitrate content in groundwater and surface water is now a threat to drinking water supply in more and more parts of the world and corrective measures are obviously needed as a matter of urgency. Any drastic restriction on the (excessive) fertilizing of agricultural land in the Netherlands is stoutly resisted by the farming sector. In the present social climate it is unrealistic to expect any worthwhile limitation on overfertilizing in the short term.

Moreover, any drastic reduction in overfertilizing would take several years to lower the nitrate content in the extracted groundwater. The fact is that by the time it reaches the extraction wells, groundwater has generally had an average underground residence time of several years. This situation forces waterworks to consider ways and means for assuring the quality of their drinking water in the immediate future. The possible options are:

- to impose restrictions on overfertilizing in protecting zones of the groundwater catchment area;
- to abstract water from another groundwater catchment area or to mix water having a high nitrate content with nitrate-free water that would have to be brought from elsewhere;
- to produce drinking water from surface water.

However, these measures are feasible in only a few situations. Consequently, the waterworks have in many situations no alternative but to remove the nitrate from the drinking water.

Processes into the removal of nitrate

A wide range of physico-chemical and biological processes are currently being developed for the removal of nitrate from drinking water. Biological denitrification processes specifically remove nitrate from drinking water while their physico-chemical counterparts are less specific and may therefore also remove other inorganic substances.

Physico-chemical processes

Ion exchange and reverse osmosis are proven techniques for removing inorganic salts. The most serious drawback to these techniques is the production of effluents in the form of brine whose disposal is often difficult so that these techniques are less commonly used. Evaporating the water from the brine to leave the salts in solid form is too costly and complicated a process to be worthwhile.[1]

Biological purification of the regenerant solution used in ion exchange with say methanol promises an appreciable reduction in the amount of brine that has to be discharged.[2] Still, this method has the disadvantage of being rather complicated.

A combination of cation and anion exchange with the dual aim of softening and nitrate removal enables regeneration to be carried out with carbon dioxide. This too can minimize the quantity of brine produced.[3]

However, anion exchange involves the risk of quaternary ammonium compounds entering the treated water. Since these compounds are suspect from the standpoint of public health, the problem clearly demands caution and attention.

Biological denitrification

Nitrate can be converted to nitrogen by bacteria in anaerobic conditions. Heterotrophic bacteria convert nitrate by making use of organic substances such as methanol, ethanol and acetic acid. The denitrification with methanol proceeds according to the following reaction:

$$5\,CH_3OH + 6\,NO_3^- \rightarrow 5\,HCO_3^- + OH^- + 7\,H_2O + 3\,N_2.$$

Autotrophic bacteria make use of inorganic substances like hydrogen and sulphur as their energy source. Denitrification with hydrogen follows the reaction:

$$5\,H_2 + 2\,H^+ + 2\,NO_3^- \rightarrow N_2 + 6\,H_2O.$$

In both processes biomass is produced as well as inorganic substances.

Autotrophic and heterotrophic bacteria both need phosphate as an essential element for their growth. In laboratory conditions the denitrification processes present no problems but little experience has yet been gained on their practical application. There are at present in Europà only a few demonstration installations where such practical experience is being obtained. Various process versions are being tested in these installations, namely:
- fluidized bed (with methanol)
- fixed bed with ethanol and/or acetic acid downflow
- fixed bed with ethanol upflow
- floating bed with ethanol upflow
- profiled lamellae (with hydrogen).

The aim of these process versions is to create within a limited space a large suface for adherence of bacteria. At the same time the flow conditions in the system are adjusted such that the mass transfer shall take place sufficiently fast. These techniques have various drawbacks, namely:

(a) they are complicated compared to the processes generally employed in groundwater pumping stations, e.g. aeration and rapid filtration;
(b) the denitrified water generally contains biodegradable matter in the form of biomass, thus demanding intensive post-treatment.

An alternative to denitrification in a treatment plant is the removal of nitrate in situ, ie. in the soil. This process is in principle free from the abovementioned drawbacks. It is also comparatively cheap. Full-scale investigations carried out by the Gelderland Eastern Water Supply Company and others have shown that the injection well employed soon becomes clogged by bacterial growth.[4] This means that the technique will only be technically possible once the clogging problem has been solved. Furthermore, with soil protection in mind, the government views the use of this technique with a rather jaundiced eye.

Reviewing the available techniques for removal of nitrate, it is apparent that none have yet proved simple, reliable and cheap in practical application over a reasonably long period of time.

Choice of process and location of investigation

Small groundwater pumping stations are mostly unmanned, generally rather basic and often of limited capacity. For removing nitrate from the groundwater handled by these pumping stations it is therefore clearly preferable to use simple processes requiring little supervision. Consequently, process selection and conduct of experiments is always geared to the need for the process to be suitable for practical application at such pumping stations.

After thorough evaluation of possible processes for the removal of nitrate from groundwater, it was concluded that biological denitrification in a fixed bed with sulphur and limestone is in principle simple, reliable and reasonably cheap.[5]

The version chosen for this process is comparable to slow sand filtration. A further requirement was that a simple secondary treatment must suffice to remove biomass from the denitrified water.

As sulphate is formed as a sideproduct the use of the sulphur/limestone process is restricted to pumping stations where the sulphate content of the raw groundwater is low enough for the sulphate standard not to be exceeded after denitrification. The Dr J. H. van Heek pumping station belonging to the Gelderland Eastern Water Supply Company meets this requirement and it was therefore decided that this should be the site for a preliminary investigation into the feasibility of the process.

The sulphur/limestone process

Principle

Autotrophic bacteria like *Thiobacillus denitrificans* are capable of converting nitrate to nitrogen in the presence of elementary sulphur according to the following reaction:

$$5\,S + 6\,NO_3^- + 2\,H_2O \rightarrow 3\,N_2 + 5\,SO_4^{2-} + 4\,H^+.$$

Beside the inorganic substances nitrogen, sulphate and hydrogen ions, biomass is also formed.

$$55\,S + 50\,NO_3^- + 38\,H_2O + 20\,CO_2 + 4\,NH_4^+ \rightarrow$$

$$4\,C_5H_7O_2N + 25\,N_2 + 55\,SO_4^{2-} + 64\,H^+.$$

Denitrification is accompanied by the formation of hydrogen ions which lowers the pH value. However, for optimal bacterial action the pH should preferably be between 6.4 and 6.8 and neutralization is therefore necessary.

For this purpose limestone granules are added to the sulphur to maintain the pH level during the process. A lot of work in this field has been done by Martin and co-workers[6,7] working with a fixed bed of limestone and sulphur. Laboratory scale experiments performed at a filtration rate of 1 m/h yielded very promising results but practical application calls for further investigations.

Pilot plant experiments (phase 1)

The following preconditions were laid down for the pilot plant experiments:
- Supersaturation with nitrogen, with consequent formation of nitrogen bubbles in the bed, should be countered.
- The loss of active biomass through backwashing of the sulphur/limestone bed should be avoided.
- The biomass and other biodegradable matter present in the denitrified water should be removable by infiltration into the soil.

In this series of pilot plant experiments nitrogen supersaturation was countered by providing a positive head of 50 kPa. At a later stage supersaturation was prevented by deaerating the untreated groundwater.

Upflow filtration is applied in order to make it easier for the nitrogen bubbles to escape assuming that this formation of these bubbles cannot be completely prevented.

Another no less important argument in favour of upflow filtration is to prevent the introduction of nitrogen and oxygen into the water.

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Summary and conclusions

(a) Investigations with a pilot plant have shown that the sulphur/limestone process combined with vacuum deaeration and infiltration of the denitrified water can offer a simple and reliable technique for the removal of nitrate from groundwater. However, the application of this technique is confined to situations where groundwater with a low sulphate content is present and infiltration is possible.

(b) The demonstration installation based on the sulphur/limestone process operated during more than four months quite satisfactorily. The process will have to show within the next 2 years whether it does indeed live up to expectation in practice.

Acknowledgements

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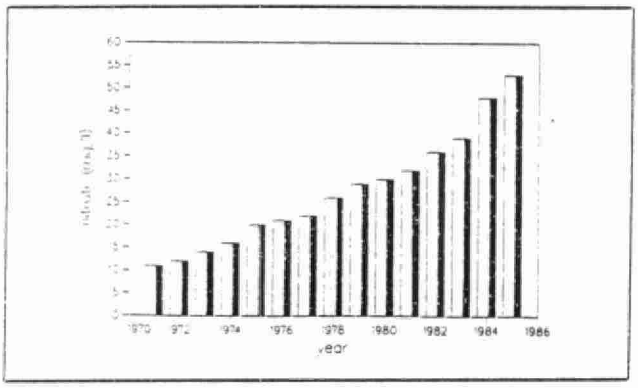

Fig. 1. Nitrate concentration in the abstracted groundwater in the Montferland over the period 1970–1986

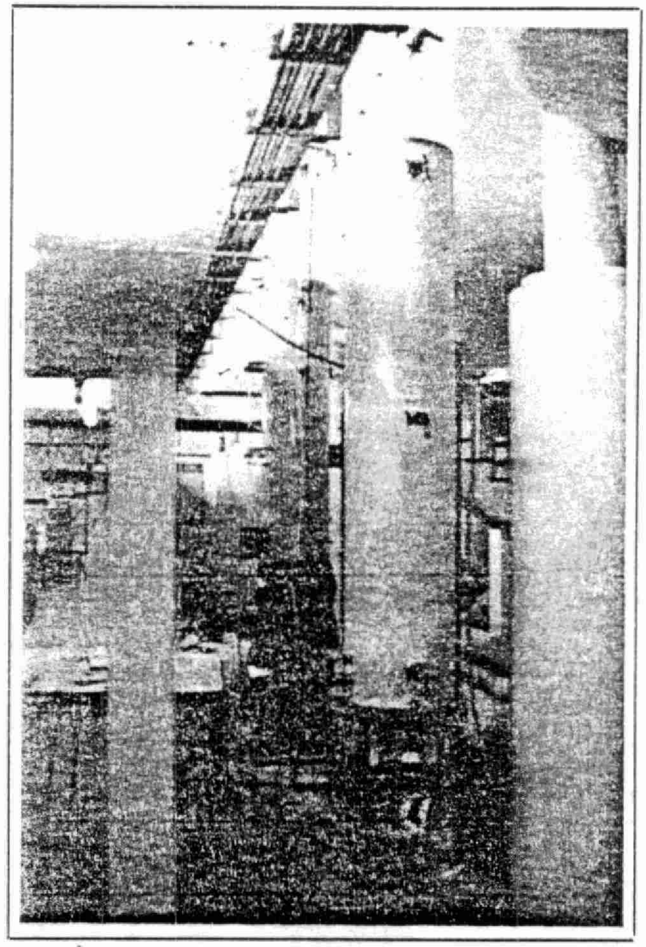

Fig. 2. The pilot plant for removing nitrate from groundwater with sulphur and limestone

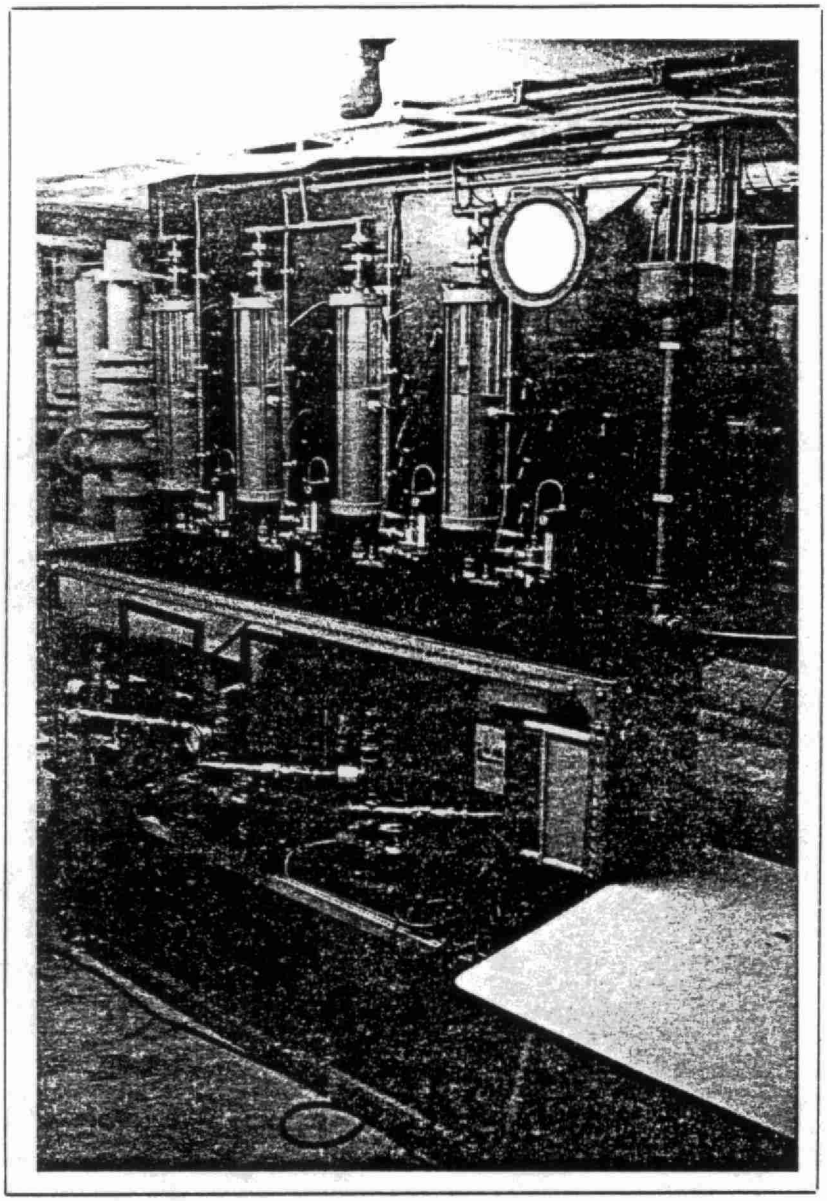

Fig. 3. The apparatus for the measurement of the artificial recharge filtration index of the denitrified groundwater

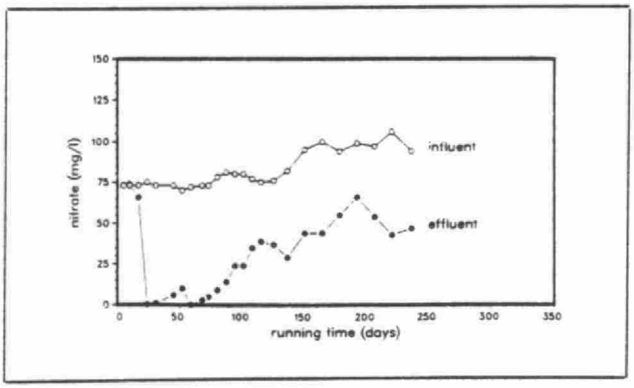

Fig. 4. The effect of slow sulphur/limestone filtration without prior vacuum deaeration

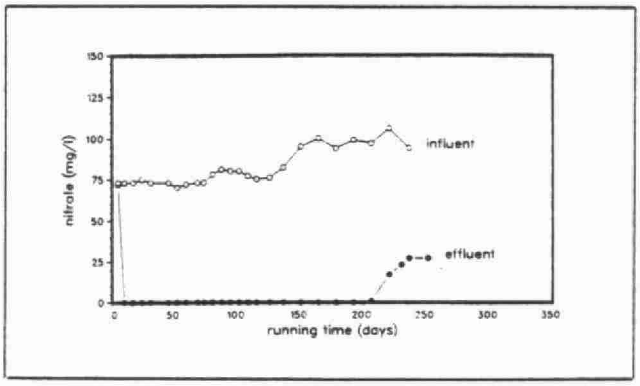

Fig. 5. The effect of slow sulphur/limestone filtration after prior vacuum deaeration

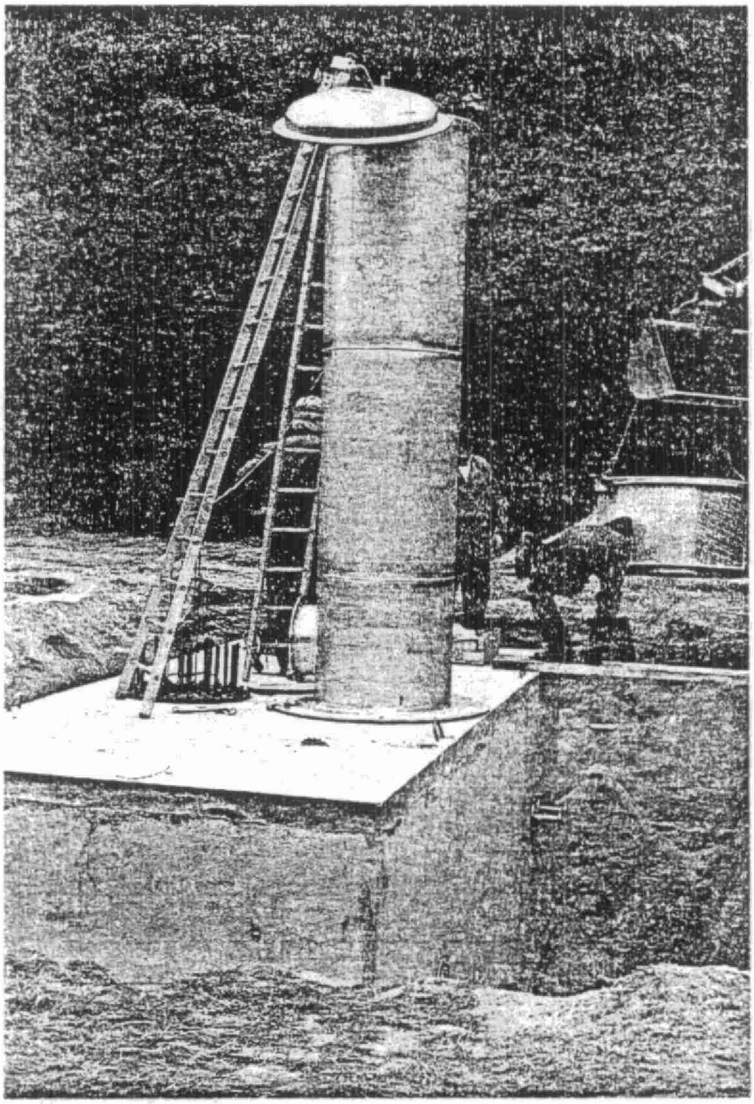

Fig. 6. The vacuum deaerator (35 m^3/h) for removal of nitrogen and oxygen from the groundwater due to be denitrified

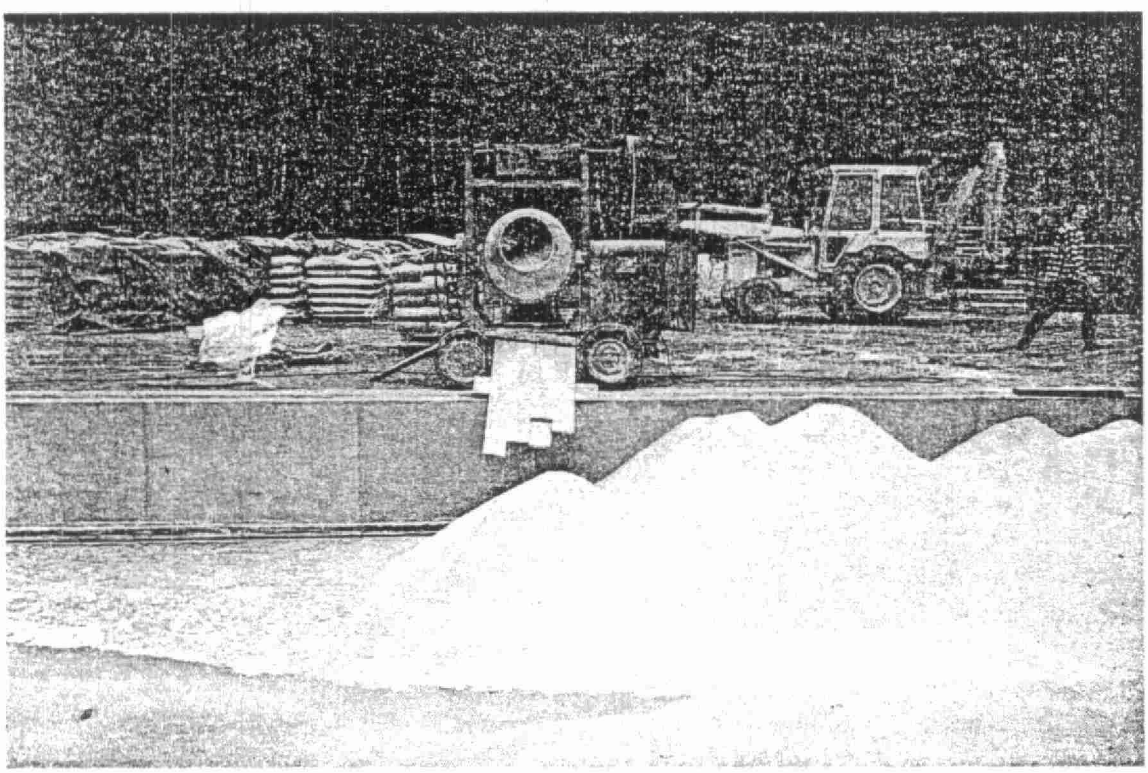

Fig. 7. The slow sulphur/limestone filter (35 m^3/h) during filling

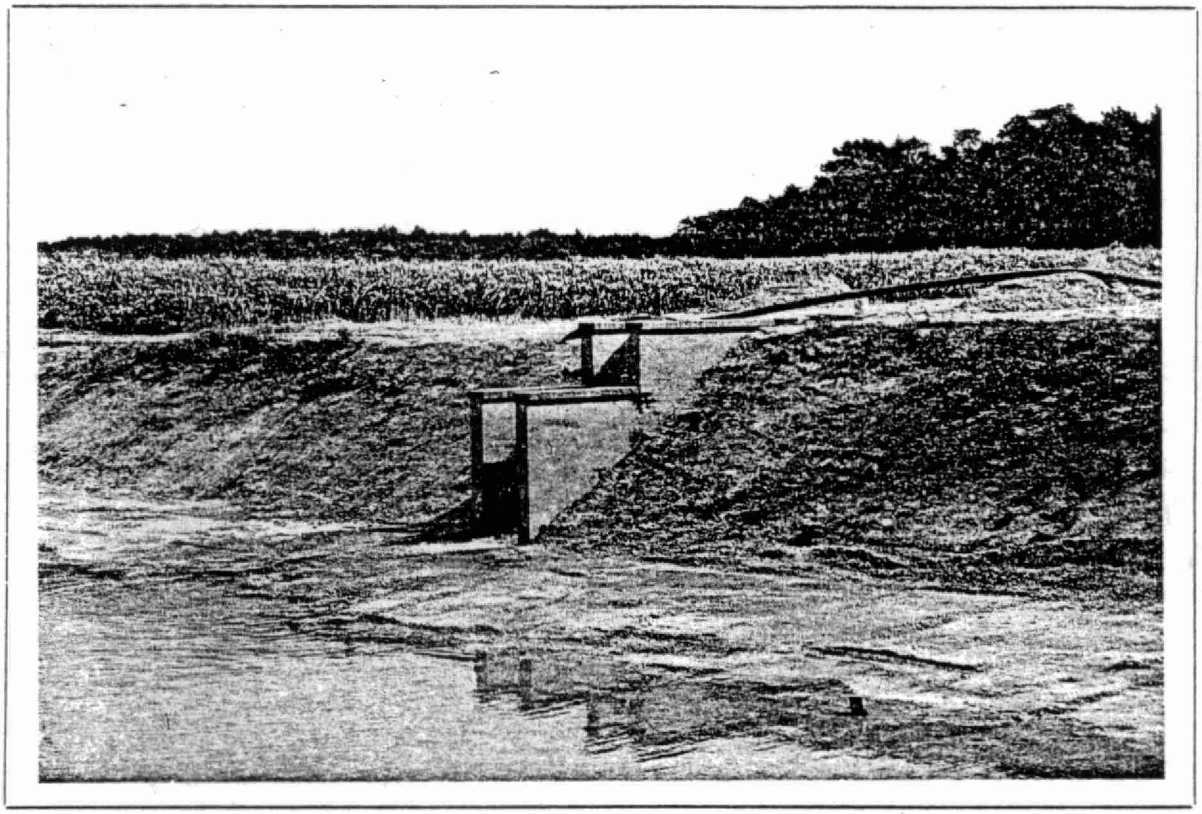

Fig. 8. The infiltration pond with cascade

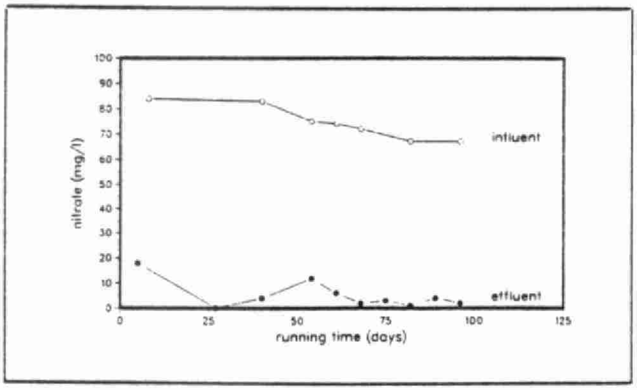

Fig. 9. The effect of the slow sulphur/limestone process on demonstration scale during the first three months of operation

EXPERIENCES WITH U.V.-DISINFECTION OF DRINKING WATER IN THE NETHERLANDS

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ABSTRACT

Since 1980 on five locations in the Netherlands Ultra Violet (UV)-installations have been introduced for the disinfection of drinking water. The reason for u.v.-disinfection on these locations is:

- removal of E.coli from groundwater
- reduction of colony counts in bank filtered water following GAC filtration
- reduction of colony counts in extensively pretreated surface water.

The effects of all three applications are illustrated with case studies. It is shown that u.v.-disinfection is a very promising technique when regrowth does not have to be restricted by a residual disinfectant. Under practical conditions u.v.-radiation produces hardly any biodegradable compounds and does not cause mutagenic activity. The costs of u.v.-disinfection vary between fl. 0,015 and fl. 0,026.

INTRODUCTION

Until 1980 no u.v.-disinfection was used for drinking water disinfection in the Netherlands. Only the Waterworks of Tilburg made use of u.v.-radiation for the disinfection of backwash water before recycling it to the treatment process.

Under normal circumstances groundwater and bank filtered water are purified by conventional treatment i.e. aeration and filtration to remove iron, manganese and ammonia. Following these processes no disinfection is needed (1). Disinfection is applied to drinking water prepared from surface water. This disinfection is carried out with chlorine and incidentally with chlorine dioxide (2).

From 1980 some changes in this policy occurred for all water types, caused by the following reasons:

Groundwater:
Incidentally disinfection is needed for drinking water prepared from groundwater. This is the case at the pumping station "De Landeus" of the Waterworks of Limburg and at the pumping station "De Tombe" of the Municipal Waterworks of Maastricht, where E.coli were detected in the finished water. Chlorination provides a good disinfection but causes many side effects (2). Besides the content of biodegradable compounds in this type of water is low, so there is no actual need for the use of a persistent disinfectant to prevent regrowth. U.V.-disinfection seems very suitable to solve this problem.
Another problem was encountered at Lauwersoog (Provincial Waterworks of Groningen) where high colony counts were found after storage of the finished water. Also for this purpose u.v.-disinfections can be applied.

Bankfiltered water:
In some cases waterworks, treating bankfiltered water with conventional treatment, have problems concerning the taste and odour of the finished water (3). Amongst others this is the case at the treatment plant in Hardinxveld of the Waterworks "Alblasserwaard en Vijfheerenlanden". To solve these problems a GAC-filtration was added to the treatment system. Especially for short running times of the carbon filters high colony counts are found in the GAC-filtrate. As for groundwater use of a persistent disinfectant to prevent aftergrowth is not needed, so once again u.v.-disinfection appears to be very suitable.

Surface water:
Following the discovery of trihalomethanes (THM)-production by drinking water chlorination (4) the Dutch waterworks and KIWA have paid much attention to the techniques to be used for surface water disinfection. Initially it was thought that post chlorination had to be maintained at the end of the treatment as a safety barrier with only a few side effects (5). However, it was established that especially post chlorination induces a high mutagenicity and causes a shift to the production of highly brominated THM (6, 7). Therefore the philosophy of the Dutch waterworks changed to:

- no chemical disinfection has to be applied when mechanical, biological and physical barriers provide water of a good (micro) biological quality
- when chemical disinfection is needed, use of alternative disinfectants should be considered. In that case chlorination must be maintained until the side effects of the alternatives have been evaluated.

For some surface water treatment plants there was no need to maintain post chlorination. Especially this was the case for waterworks with at least a double filtration step. These waterworks proved to produce water with low contents of biodegradable compounds. When the final filtration step was a slowsand filtration the colony counts were very low so post disinfection could be omitted completely (8, 9). When carbon filtration was the final treatment step colony counts proved to be relatively high.

U.V.-disinfection is very suitable to reduce these colony counts. This option is not in operation until now, but is investigated extensively at the Zevenbergen plant of the Waterworks of North West Brabant at pilot plant scale.

The developments described in this section have led to either the use or the study of u.v.-disinfection in the Netherlands' drinking water practice. In this paper we will present a casy study for each water type:

- Removal of E.coli by u.v.-disinfection from groundwater. Full scale application at "De Landeus" carried out by the Waterworks of Limburg together with the Laboratory of the Southern Netherlands Waterworks.
- Reduction of colony counts by u.v.-disinfection from treated bank filtered water. Pilot investigation and full scale application at Hardinxveld carried out by the Waterworks "Alblasserwaard en Vijfheerenlanden" and KIWA.
- Reduction of colony counts by chlorination, slowsand filtration and u.v.-disinfection of treated surface water. Pilot investigation carried out at Zevenbergen by the Waterworks of North West Brabant, the Laboratory of the Southern Netherlands Waterworks and KIWA.

In all investigations the effect has been determined by measurements of E.coli, bacteria from the coligroup or colony counts.
In the last two investigations attention has also been paid to the possible side effects of the disinfection step. This concerns the production of biodegradable compounds and the formation of mutagenic activity.
Finally attention is paid to the costs of the treatment step.

U.V.-DISINFECTION OF GROUNDWATER

The water to be treated origins from two captations being "De Landeus" with an average capacity of 50 m^3/h and "The Nuthbron" with an average capacity of 30 m^3/h. Up to 1980 the water was distributed without any treatment. Early 1980 bacteria from the coligroup and E.coli were detected in both captations. Initially the problem was solved by a chlorine dosage. For a long term solution it was decided to apply u.v.-disinfection. April 1980 two u.v.-disinfectors type Beluva HD/50 were installed. Both disinfectors are provided with one high pressure burner in a quartz tube. The apparatus is equipped with a monitor for the registration of the u.v.-dose (relative measurement) and with a wiper to remove deposits on the quartz tube.

The disinfectors have been used in the production of drinking water from April 1981. The results for the period 1981-1985 based on reduction of plate counts PCA 37°C and removal of bacteria from the coligroup and E.coli are summarized in Table 1.

Table 1 Effect of u.v.-disinfection at De Landeus (period 1981-1985)

Year	Number of measurements	Plate count PCA 37°C >10		Bact. coligroup pos.		E.coli pos.	
		before u.v.	after u.v.	before u.v.	after u.v.	before u.v.	after u.v.
1981	25	1	0	13	0	11	0
1982	42	1	0	27	2	12	0
1983	48	6	0	35	6	18	3
1984	42	10	3	29	2	25	2
1985	12 before u.v. 32 after u.v.	1	0	12	0	-	-

Out of about 200 measurements, 116 times bacteria from the coligroup were detected in the raw water from which 65 could be confirmed as E.coli. After u.v.-disinfection 10 times bacteria from the coligroup could be detected from which 5 could be confirmed as E.coli.
In most cases all coli are destructed by u.v.-radiation. In a few cases no complete removal was achieved caused by a too low u.v.-dose. Reason for this low u.v.-dosage was twofold:

- in three cases the u.v.-monitor was malfunctioning, indicating a higher dosage than actually present. From that moment the monitor reading was checked regularly with a mV-meter
- in two cases the u.v.-dosage was experimentally lowered below 57 % of the initial dosage (from ~ 40 mWs/cm^2 to 23 mWs/cm^2). Then u.v.-breakthrough of E.coli started to occur. Coli were removed by a temporary post-chlorination.

After checking the monitor reading and replacing u.v. burners at 60 % of the original u.v.-energy (24 mWs/cm^2) no breakthrough occurred anymore.

It is obvious that the u.v.-intensity drops as a function of the burning time. In the period 1981-1985 15 burners were used with a burning time of 900-11,700 hours (average 4,145 hours). The manufacturer claims that switching on and off does not influence the lamp life. However this seems not to be the case.

Finally a calculation has been made for the costs of u.v.-disinfection under these conditions.
The investment in 1980 amounted to ƒ 42,690.-- including electrotechnical and mechanical modifications by the waterworks. For a depreciation in 15 years and based on an interest of 10 % this amounts to fixed costs of fl. 4,980/year.
The variable costs are concerned with the replacement of burners, quartz tubes and maintenance. For 1985 this amounts to fl. 1,170.--. The second part of the variable costs concerns the energy consumption. In 1985 45,000 kWh was consumed, amounting to about fl. 6,000.--.
This brings the total cost of the u.v.-disinfection for 1985 up to fl. 12,150.-- for a total production of 730,000 m^3 (84 % of the design capacity of the u.v.-disinfection). U.V.-disinfection of 1 m^3 of water costs fl. 0.017. The cost aspects are summarized in Table 2.

Table 2 Costs of u.v.-disinfection at De Landeus (1985)

	Cost/year	Cost/m^3 water
Depreciation	fl. 4,980.--	fl. 0.007
Maintenance	fl. 1,170.--	fl. 0.002
Energy consumption	fl. 6,000.--	fl. 0.008
Total costs	fl. 12,150.--	fl. 0.017

U.V.-DISINFECTION OF BANKFILTERED WATER

The water to be treated at Hardinxveld is bank well filtered water from the river Rhine. Up to 1983 90-180 m^3/h were treated according to the following purification system:

bankwell filtered water abstraction → aeration → not submerged filtration → aeration → rapid filtration

Gradually the finished water gave rise to taste and odour complaints. For that reason the Waterworks "Alblasserwaard en Vijfheerenlanden" decided to remove taste and odour with GAC-filtration. Pilot investigations showed excellent results; the only problem being relatively high colony counts (PCA 22°C) especially for short filter runs.
In a participating investigation with KIWA the disinfection of the GAC-filtrate was investigated in a pilot installation. Especially u.v.-disinfection showed satisfactory results. Some results over 1982 are presented in Table 3 for a GAC pilot filter with a carbon life of about 2 years.

Table 3 Effect of u.v. disinfection at Hardinxveld (pilot investigation, 1982)

Date	Plate count PCA 22°C	
	before u.v.	after u.v.
17-2	80	0
24-2	80	0
17-3	35	0
24-3	10	1
31-3	7	1
7-4	100	5
14-4	10	4
21-4	25	2
28-4	25	3
4-5	8	0
12-5	40	1

Although the colony counts in de carbon filtrate were very low, a good reduction was achieved.
Therefore in 1982 it was decided to modify the treatment system by adding a GAC-filtration and an u.v.-disinfection to:

bankwell filtered water abstraction → aeration → not submerged filtration → aeration → rapid filtration

aeration → GAC-filtration → u.v.-disinfection

The GAC-filtration is carried out with Norit ROW 0.8S with an empty bed contact time of 15-30 minutes. U.V.-disinfection is applied with a Beluva HD-100/4-type disinfector, with a fixed u.v.-dose of at least 20 mWs/cm^2. The apparatus is equipped with four high pressure burners in quartz tubes. Each burner has his own u.v.-monitor. Depending on water flow and water quality the u.v.-dosage is produced by one or more burners. The highest u.v.-dosage is 30 mWs/cm^2, the lowest dosage is 20 mWs/cm^2. Each u.v.-burner/quartz tube is equipped with a wiper. The results for the period 1983/1984 are presented in figure 1 a and b for plate counts PCA 22°C and in figure 2 for special plate counts LLA 1.0 (10).

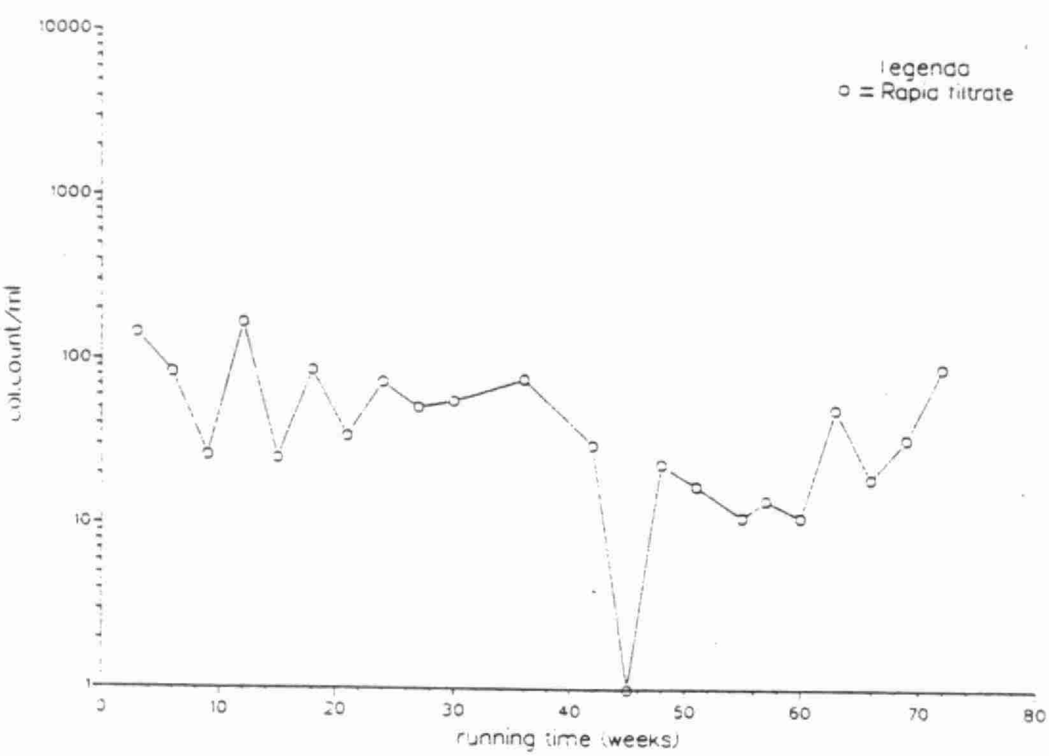

Figure 1a Plate count PCA (22°C) in rapid filtrate

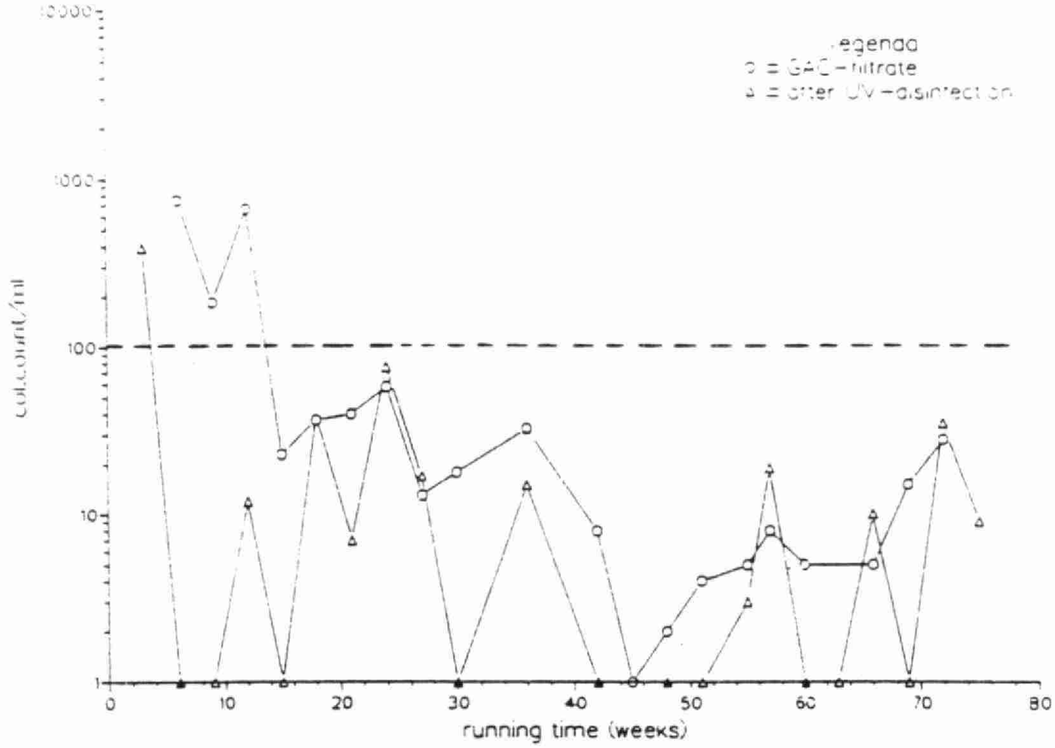

Figure 1b Plate count PCA (22°C) in GAC-filtrate before and after u.v.-disinfection

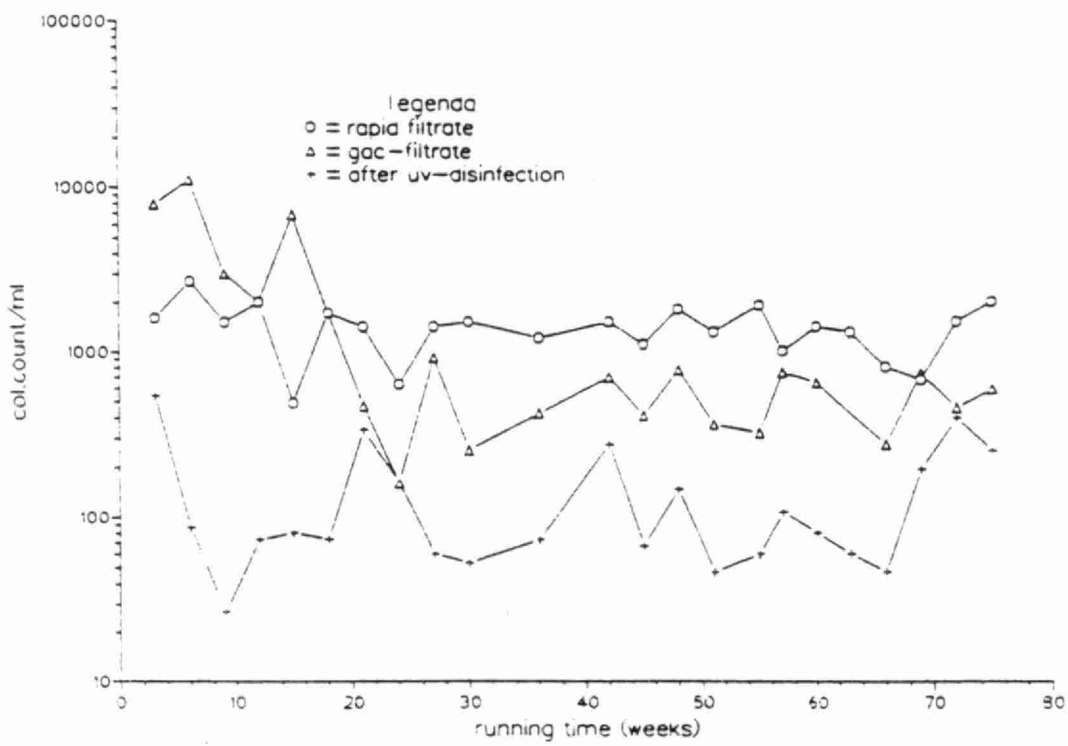

Figure 2 Special plate count (LLA 1.0) in rapid filtrate and in GAC-filtrate before and after u.v.-disinfection

The standard plate count PCA 22°C in rapid filtrate is always lower than 100/ml. In the GAC-filtrate the first 15 weeks of the filter run the colony count is higher than 100/ml. U.V.-disinfection gives a reduction to an average colony count of about 10/ml.
The effect of u.v.-disinfection is once more illustrated with the effect on the plate count LLA 1.0. A fixed u.v.-dose of about 20-30 mWs/cm^2 gives a reduction with a factor of 10-15. From the figures it can be seen that the results achieved are very satisfactory. Always the colony count is lower than the drinking water standard (100/ml).

Two potential hazardous effects of u.v.-disinfection are the production of biodegradable compounds and the formation of mutagenic activity. Both phenomena have been studied. Production of biodegradable compounds has been characterized with the help of the AOC (assimilable organic carbon) determination (11). The results are presented in Table 4.

Table 4 AOC-content (μg AcC/l) in rapid filtrate and GAC-filtrate before and after u.v.-disinfection

Filter run (weeks)	AOC (μg Ac C/l)		
	rapid filtrate	GAC-filtrate	after u.v.
3	4,5	2,0	2,8
9	3,2	2,0	2,2
15	6,9	4,4	7,0
21	2,7	1,7	1,9
27	3,6	1,6	1,6
36	4,7	3,7	4,5
48	5,0	3,6	3,9
60	5,3	4,3	4,4
72	1,7	3,8	5,2

From the Table it can be seen that the AOC-content of the GAC-filtrate gradually rises from 2 to 4 μg Ac C/l. The AOC-content after u.v.-disinfection is of the same magnitude or only slightly higher. These contents do not give any rise to regrowth.

Finally the mutagenicity in the Amestest has been determined. During the whole period no mutagenicity was found before and after u.v.-disinfection, so under these conditions u.v.-disinfection does not induce mutagenicity.
A calculation has been made for the costs of u.v.-disinfection under these circumstances.
The investment in 1983 amounted to fl. 74,800.-- including electrotechnical and mechanical adaptations of the waterworks. For a depreciation in 15 years and for an interest of 10 % this amounts to annual fixed costs of fl. 8,727.--. The variable costs concern mainly the replacement of u.v.-burners (fl. 1,632/year). Costs for quartz tubes and maintenance can be neglected. The annual energy consumption (1983/1984) is 36,000 kWh amounting to fl. 10,612.--.
This brings the total annual costs of the u.v.-disinfection for 1983/1984

up to fl. 19,339.-- for a total water production of 811,000 m^3 (46 % of the design capacity of the u.v.-disinfector). So u.v.-disinfection of 1 m^3 of water costs fl. 0.024. The cost aspects are summarized in Table 5.

Table 5 Costs of u.v.-disinfection at Hardinxveld (1983/1984)

	Cost/year	Cost/m^3 water
Depriciation	fl. 8,727	fl. 0.011
Maintenance	fl. 1,632	fl. 0.002
Energy consumption	fl. 8,990	fl. 0.011
Total costs	fl. 19,339	fl. 0.024

U.V.-DISINFECTION OF SURFACE WATER

The water to be treated at Zevenbergen is surface water of the river Meuse after storage in the Biesbosch. About 300 m^3/h is treated according to the following purification system:

Transport chlorination (in summer) → Coagulation → Flotation → Breakpoint chlorination →

Dual media filtration → GAC-filtration → Postchlorination

Chlorination and especially post chlorination cause a high mutagenicity, high contents of adsorbable organohalogens and postchlorination of extensively treated water causes a shift to the production of brominated THM (6, 7, 12). Therefore alternatives for chlorination have been investigated.
In this paper we will only discuss the suitability of slow sand filtration and u.v.-disinfection as alternatives for postchlorination under maintenance of transport chlorination (in summer) and breakpoint chlorinations. Additional results without a preceeding chlorination will be published elsewhere.

Slow sand filtration has been applied with a linear velocity of 0.5 m/h. U.V.-disinfection has been carried out with a Beluva D1-type disinfector. The apparatus is equipped with one low pressure burner in a quartz tube. The apparatus has a monitor for a relative measurement of the u.v.-dosage. The manufacturer claims a maximum capacity of 1,6 m^3/h for an initial u.v.-dose of 40-45 mWs/cm^2 with an u.v.-transmission of the water of 100 %. The experiments were carried out with 3,5 m^3/h for the first 50 weeks and with 6,0 m^3/h the final 25 weeks corresponding with an initial dose of 20,6 mWs/cm^2 and 12,0 mWs/cm^2 respectively for water without u.v.-absorbing compounds.
The effects of chlorination, u.v.-disinfection and slow sand filtration are illustrated in figure 3 for the logarithmic reduction of plate counts LLA 1.0 (10).

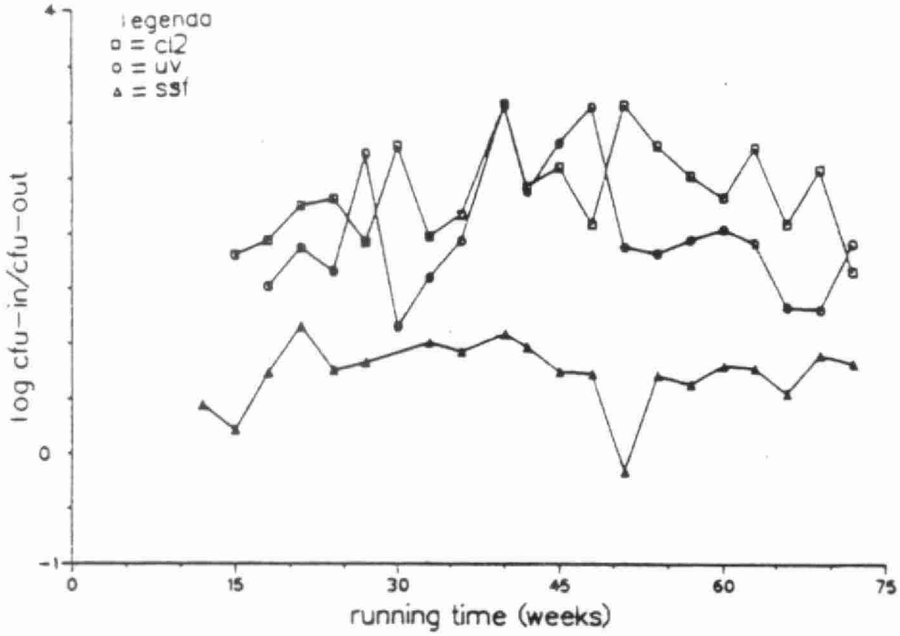

Figure 3 Logarithmic reduction of plate counts LLA 1.0 by chlorination, u.v.-disinfection and slow sand filtration

From figure 3 it can be seen that slow sand filtration gives by far the worst results. Best results are obtained by chlorination, closely followed by u.v.-disinfection.
From these results it may be concluded that u.v.-disinfection provides a good alternative for post-disinfection. For that reason we will focus on this alternative. The plate counts PCA 22°C before and after u.v.-disinfection together with the logarithmic reduction are presented in figure 4a and b, the plate counts LLA 1.0 before and after u.v.-disinfection together with the logarithmic reduction in figure 5a and b.

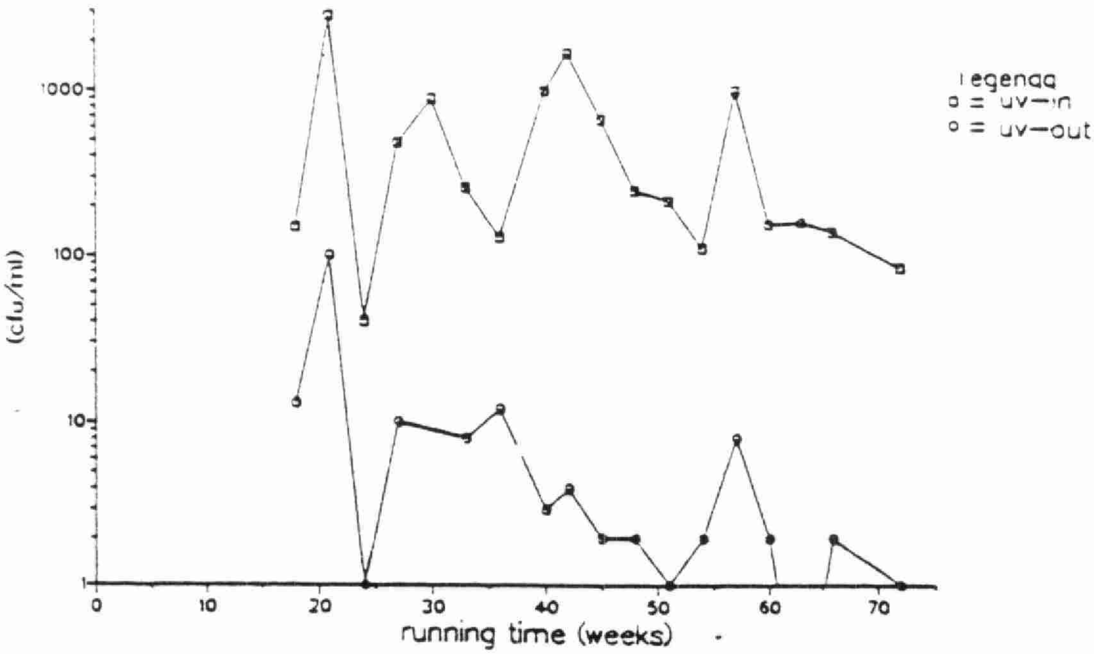

Figure 4a Plate counts PCA 22°C before and after u.v.-disinfection

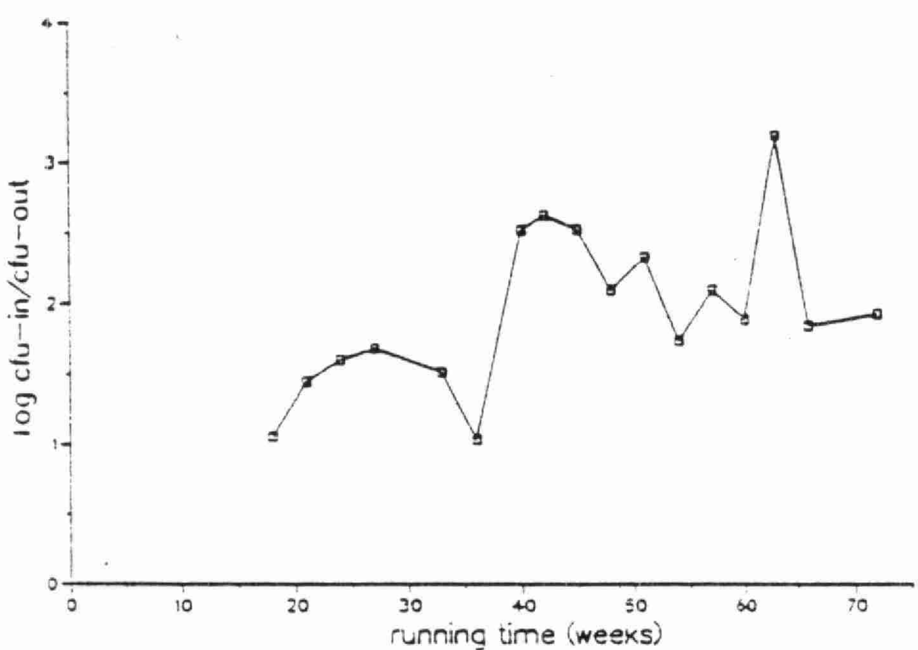

Figure 4b Log reduction of plate counts PCA 22°C by u.v.-disinfection

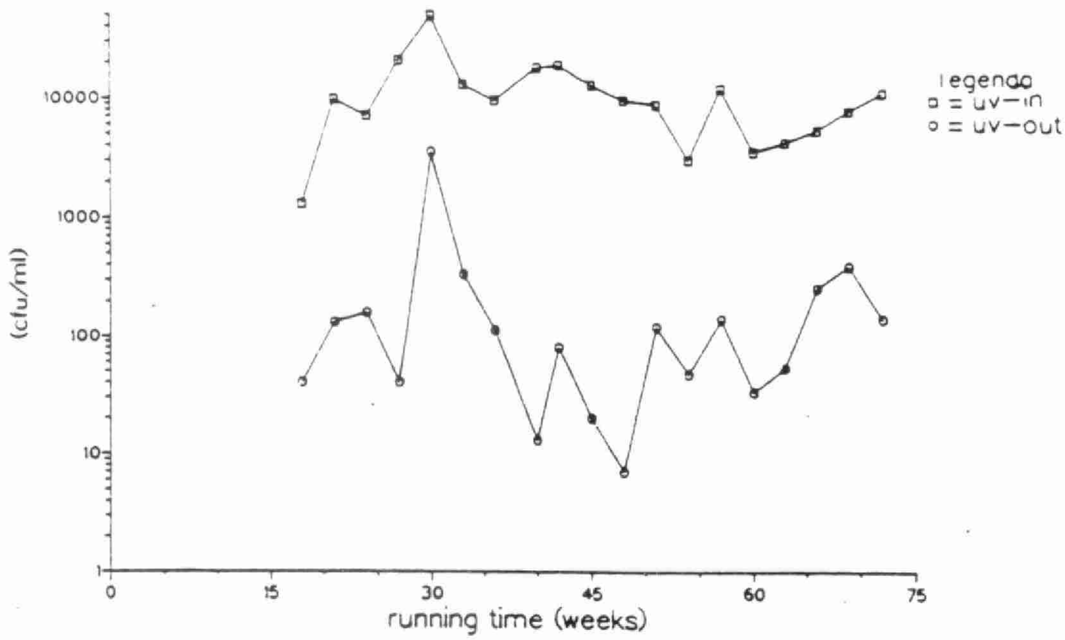

Figure 5a Plate counts LLA 1.0 before and after u.v.-disinfection

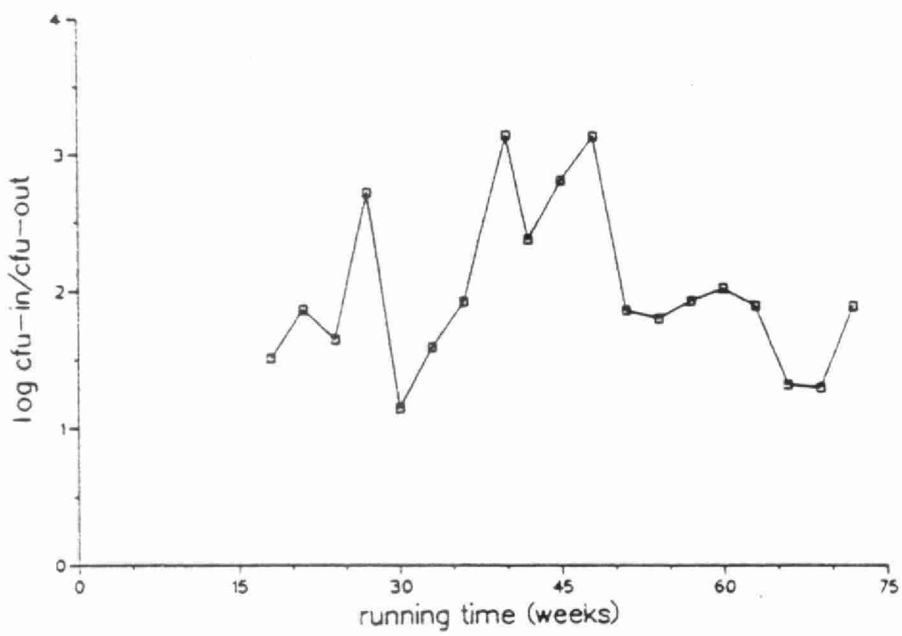

Figure 5b Log reduction of plate counts LLA 1.0 by u.v.-disinfection

For both plate counts a good reduction is achieved by u.v.-disinfection. There is no significant change in the removal after 50 weeks when the throughput was raised from 3,5 m^3/h to 6.0 m^3/h. This is illustrated once more in Table 6.

Table 6 Log removal of plate counts PCA 22°C and plate counts LLA 1.0

Per week nr.	Log removal PCA 22°C min.	max.	avg.	Log removal LLA 1.0 min.	max.	avg.
<50	-3,3	4,5	1,5	1,1	3,1	2,2
>50	-0,8	3,3	1,4	1,3	2,0	1,8

To characterize the side effects of the disinfection steps AOC-determinations and Amestesting have been carried out. AOC-contents of the GAC-filtrate are low. Chlorination causes a rise of the AOC-content, u.v.-disinfection does not influence the AOC-content.
Marked differences have been found for the mutagenicity in the Amestest. As expected chlorination gives a significant rise in the mutagenicity. U.V.-disinfection shows no effect on this parameter.

A rough calculation has been made for the cost of u.v.-disinfection under these conditions (see Table 7).

Table 7 Costs of u.v.-disinfection at Zevenbergen at pilot plant scale (1984)

	Cost/year	Cost m^3 water $\emptyset = 3,5\ m^3/h$	$\emptyset = 6\ m^3/h$
Depreciation	fl. 422.50	fl. 0.014	fl. 0.008
Maintenance	fl. 310.--	fl. 0.010	fl. 0.006
Energy consumption	fl. 62.43	fl. 0.002	fl. 0.001
Total costs	fl. 794.93	fl. 0.026	fl. 0.015

It must be emphasized that these costs cannot be compared directly to the costs of the full scale installations.

EVALUATION AND DISCUSSION

In this paper three case studies about u.v.-disinfection of different water types have been presented. From these case studies the following conclusions can be drawn:

- U.V.-disinfection can be used for the kill of E.coli in ground water. The process proves to be effective at a minimum u.v.-dose of about 24 mWs/cm^2. The costs of the process amounts to fl. 0.017/m^3 of water.
- U.V.-disinfection is suitable for the reduction of colony counts in GAC-filtered bank filtered water. At an u.v.-dosage of 20-30 mWs/cm^2 plate counts PCA 22°C are never higher than 100 ml. Presumably the u.v.-dose needed for disinfection can be even lower, especially for periods when the carbon life is relatively long.

U.V.-disinfection with doses of 20-30 mWs/cm^2 does not produce mutagenic compounds and does not give rise to regrowth. The costs of the process are fl. $0.024/m^3$ water.

- U.V.-disinfection is a good alternative for post chlorination of extensively treated surface water. For initial u.v.-dosage of 12 and 20 mWs/cm^2 good reductions for plate counts PCA 22°C are achieved. Once again u.v.-disinfection does not cause regrowth and does not induce mutagenic activity. Based on pilot plant calculations the costs vary between fl. 0.015 and fl. $0.026/m^3$ water.
- The apparatus for u.v.-disinfection can be handled very easily. The major drawback at this moment is the monitoring of the u.v.-dosage. No absolute measurements are provided by the manufacturer at this moment, while the relative measurement must be checked regularly for malfunctioning.

From the preceeding it may be clear that u.v.-disinfection is a very useful technique for disinfection of all types of drinking water under the following restrictions:

- The water must have a low concentration of biodegradable compounds, so regrowth will not occur.
- The distribution mains does not need any protection of an disinfectant.
- The u.v.-absorbtion of the water must not be extremely high (costs).

When these requirements are met u.v.-disinfection can be used with good results at relatively low costs.
More information is needed about the effective u.v.-dosage and especially about the monitoring of this u.v.-dosage.

ACKNOWLEDGEMENT

The authors want to express their thanks to A.J.H.F. Creusen (Waterworks of Limburg) for placing the results obtained at the pumping station "De Landeus" at their disposal.
The Hardinxveld data are obtained in an investigation of the Waterworks "Alblasserwaard en Vijfheerenlanden" and KIWA. The authors thank P.K. Giethoorn, Ing. R.C.G. de Koning and W. Ambachtsheer for their participation in this project.
The Zevenbergen data are obtained in an investigation of the Waterworks of North West Brabant, the Laboratory of the Southern Netherlands Waterworks and KIWA. The authors thank Ir. P. v. Tartwijk, Ir. G. Zoet, Ir. P.A.N.M. Nuhn, F.A.P. Houtepen and Drs. L.A.C. Fey for their coöperation.

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SCANNADIA

SCANDINAVIA

EMERGING WATER SUPPLY TECHNOLOGY

AWWARF Code #: SC-01

PROJECT DESCRIPTION

Project Title:

Water Treatment for Combined Humics Removal and Corrosion Control.

Contact (name of person, organization, address, telephone):

Bjørnar Eikebrokk

Project Description (Please attach a schematic diagram if appropriate):

Fine graded calcium carbonate (98% $<$ 2 µm) in a stable slurry form (75% solids) is used for corrosion control. The dissolution rate of calcium depends primarily on particle size and pH. By removing humis at low pH (adsorption/charge neutralization) in the first filter in a two-filter-inseries-system, the conditoins are excellent for $CaCO_3$-addition to the second filter, undissolved $CaCO_3$-particles are retained in the filter until dissolution or backwash. In this way the water quality standards for corrosion control (Ca, Alk.) are full-filled without using CO_2 at all. Residual alum from the coagulation of humics is also removed in the second filter.

Operating and cost data (including data on efficiency, results, etc.):

Yet not available.

Place(s) of installation/application (including dates):

Pilot scale.

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

EMERGING WATER SUPPLY TECHNOLOGY

AWWARF Code #: SC-02

PROJECT DESCRIPTION

Project Title:

Water Treatment for Corrosion Control Using Calcium Carbonate Slurry and Carbon Dioxide.

Contact (name of person, organization, address, telephone):

Bjørnar Eikebrokk, NORWAY

Project Description (Please attach a schematic diagram if appropriate):

Calcium carbonate slurry and carbon dioxide gas is added to the water before the water is filtered through an anthracite sand dual media filter. Only a small flow ($<10\%$) is treated this way. By using high $CaCO_3$ and CO_2 doses, the turbidity-free filter effluent is mixed into the total water flow to meet corrosion control water quality standards.

Operating and cost data (including data on efficiency, results, etc.):

Investment costs are estimated to US $ 0.017 per m^3 water treated. Chemical costs are estimated to US $ 0.023 per m^3 water treated. The figures are valid for a treatment plant capacity of 70-80 m^3 per hour.

Place(s) of installation/application (including dates):

Pilot/full-scale.

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

EMERGING WATER SUPPLY TECHNOLOGY

AWWARF Code #: SC-03

PROJECT DESCRIPTION

Project Title:

Humic Substance Removal by Direct Filtration

Contact (name of person, organization, address, telephone):

Bjørnar Eikebrokk, NORWAY

Project Description (Please attach a schematic diagram if appropriate):

Direct filtration for humics removal has been tested for a period of several years, both in lab-scale, pilot-scale and full-scale treatment plants. The process is well suited for raw waters high in colour (40-50 mg Pt/l), but low in turbidity (<1 NTU).

Operating and cost data (including data on efficiency, results, etc.):

Investment costs (1987) are US $ 219,000 and US $ 625,000 for plants with capacities of 25 and 250 m^3/h, respectively. The corresponding total costs are estimated to be US $ 0.18 and US $ 0.06 per m^3 water treated.

Place(s) of installation/application (including dates):

Full-scale operation

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

EMERGING WATER SUPPLY TECHNOLOGY AWWARF Code #: SC-04

PROJECT DESCRIPTION

Project Title:

Rapid detection of coliform and heterotrophic bacteria using fluorogenic substrates.

Contact (name of person, organization, address, telephone):

James D. Berg and Liv Fiksdal
Aquateam - Norwegian Water Technology Centre
P.O. Box 6593 Rodeløkka
0501 OSLO 5
47-2-371300

Project Description (Please attach a schematic diagram if appropriate):

Three fluorogenic methylumbelliferone (MU) substrates were evaluated for rapid detection of total and fecal coliform bacteria (TC and FC) in drinking water. 4-MU-B-D-galactoside, MU-heptanoate and MU-glucuronide were used to determine enzyme activity as a surrogate measure of coliform concentration. Coliforms occuring in river water and in potable water artificially contaminated with raw sewage were tested. The initial rate of hydrolysis (F) of MU-B-D-galactoside shows promise as an indicator of TC and FC within 15 min. F of MU-glucuronide was insufficient in the 15 min assay and combinations of the MU-substrates did not enhance F. A direct membrane filter method incorporating MU-B-D-galactoside into an agar medium allowed the detection of as few as 1 FC/100 ml within 6 h.

Operating and cost data (including data on efficiency, results, etc.):

The results suggest that coliforms in the range of 60-100 CFU/100 ml can be detected by fluorometry within 15 min with the same precision attainable by MPN procedures. The method utilizes relatively inexpensive equipment, a water bath and a flurometer, and can be automated. The direct MU 6h MF method permits counting as few as 1 FC/100 ml in 6 hours and requires only a hand-held long wave UV lamp to visualize colonies.

Place(s) of installation/application (including dates):

Field and lab tested in Trondheim, Norway.

Patent staus, if applicable:

U.S. Patent pending (Nov. 1987).

Other information (e.g., funding source, cooperating agencies, etc.):

Royal Norwegian Council for Scientific and Industrial Research (NTNF)
The World Bank McNamara Fellowship Program.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

aquateam norwegian water technology centre as

Enzymic Hydrolysis of Fluorogenic Substrates to Rapidly Detect Microbial Contamination

by

James D. Berg
Aquateam A/S
P.O.Box 6326 Etterstad
0604 Oslo 6
NORWAY

and

Liv Fiksdal
Norwegian Institute of Technology
7034 Trondheim-NTH
NORWAY

Presented at
Emerging Technologies, Phase III
Venice, Italy
May, 1988

Sponsored by
AWWA

INTRODUCTION

Conventional microbiological analyses of drinking water for coliform bacteria require 24 to 72 hours to complete. The elapsed time is too great to provide useful information about a decrease in quality that may require immediate remedial measures. Hence, the first reason for the development of a rapid method is to protect the public health, especially in cases where contaminated sources or interrupted treatment can occur. It has been reported that of the 38 waterborne disease outbreaks or 10 000 ilnesses per year in the USA, 80 per cent were attributable to water system deficiencies. Furthermore, rapid methods have the potential to be less costly than conventional by reducing labor costs, especially if they can be automated. Lastly, rapid methods could be used for monitoring and controlling treatment processes such as disinfection or sand filtration.

The objective of the present study was to evaluate the use of the enzymic hydrolysis of fluorogenic substrates as rapid methods for detecting fecal contamination of water. Guidelines for the research were to: 1) improve upon the time and/or sensitivity limits given for the rapid methods reported in Part 919, Standard Methods (APHA, 1985); 2) use common and relatively inexpensive instruments and reagents; 3) develop procedures that ultimately can be automated.

RESEARCH APPROACH

During the past two years several rapid methods have been investigated at the Norwegian Institute of Technology (NTH). Two methods have been developed which determine bacterial concentrations by measuring the activity of a particular group of enzymes. A so-called fluorogenic substrate (non-fluorescent) is mixed with a water sample. Metabolically active bacateria that have the appropriate enzymes can hydrolyze the substrate yielding a fluorescent product (Fig. 1) The rate of product formation (ΔF), for some groups of aerobic heterotrophs, can be measured accurately within 20 min. As shown in Fig. 2, an fluorescent umbelliferone derivative is produced by the B-D-galactosidase enzymes in coliform group bacteria at a constant rate. The methods have been filed with the U.S. Patent Office.

RESULTS

The rate of hydrolysis (ΔF) can be compared with bacterial counts by conventional methods requiring 24 h to complete (Fig. 3). In this manner a simple and inexpensive method yields the same information in 20 min instead of 24 hours (8). A similar method has been developed for determining non-specific hetrotrophic activity in water as well, using the lipase-esterase group of enzymes to hydrolyze 4-methylumbelliferone heptanoate (Fig. 4).

The aforementioned surrogate measurement of the presence of coliforms is promising, but presently lacks the sensitivity required for monitoring drinking water. Therefore a second, direct counting method was developed in which fluorescing microcolonies are detected. The method requires $\leq$ 6h to detect I CFU of total or fecal coliforms per 100 ml.

SUMMARY

1. HPC in drinking water can be determined indirectly by monitoring ΔF of 4-MU-heptanoate fluorometrically. A detection limit of ca. 100-500 HPC/ml is achievable within 20 min.

2. Coliform bacteria (FC or TC) can be detected indirectly by monitoring ΔF of 4-MU-B-D-galactoside fluorometrically. A detection limit of ca. 60-100 TC/100 ml is achievable within 20 min.

3. Direct detection of FC using an MF method allows detection of 1 FC/100 ml in 6 hours.

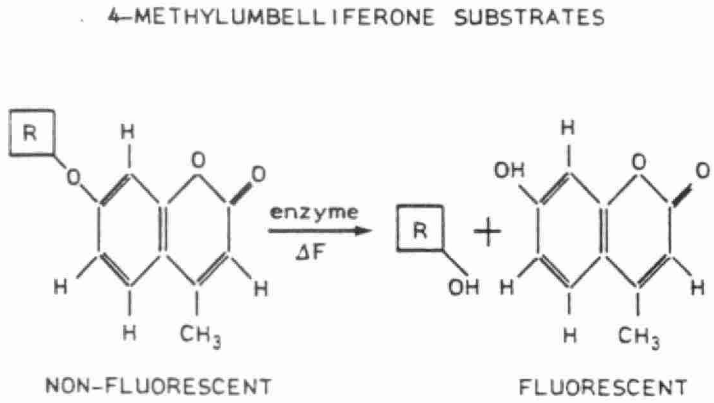
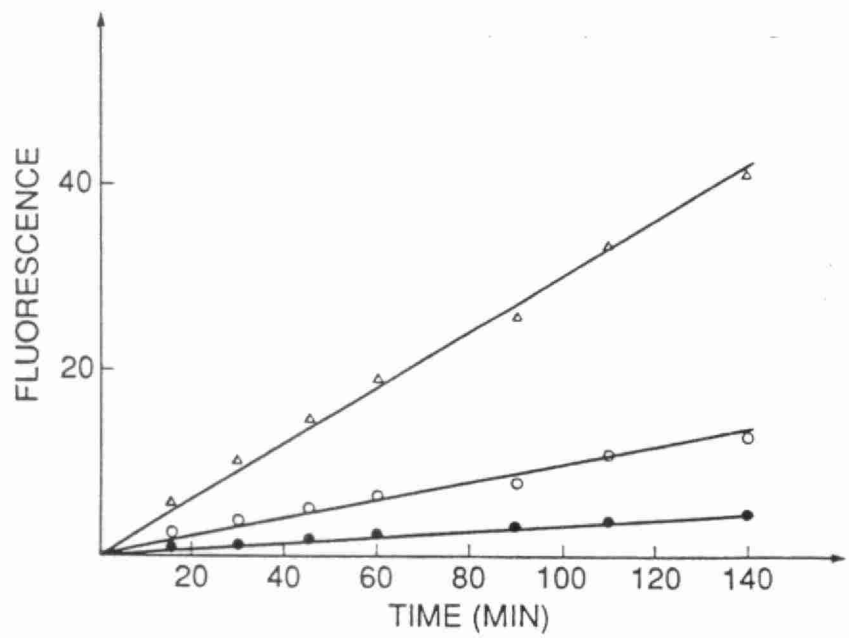


Figure 1. Production of fluorescent product by enzymatic hydrolysis of a fluorogenic substrate.



Figur 2. Production of methylumbelliferone from 4-MU-B-D-galactoside by coliform bacteria in drinking water contaminated with raw sewage (•). Addition of lactose enhanced induction of B-D-galactosidase (o). Addition of sodium lauryl sulfate, a common selective ingredient for coliforms, further enhanced activity (Δ). Enzyme assay temperature = 41.5°C.

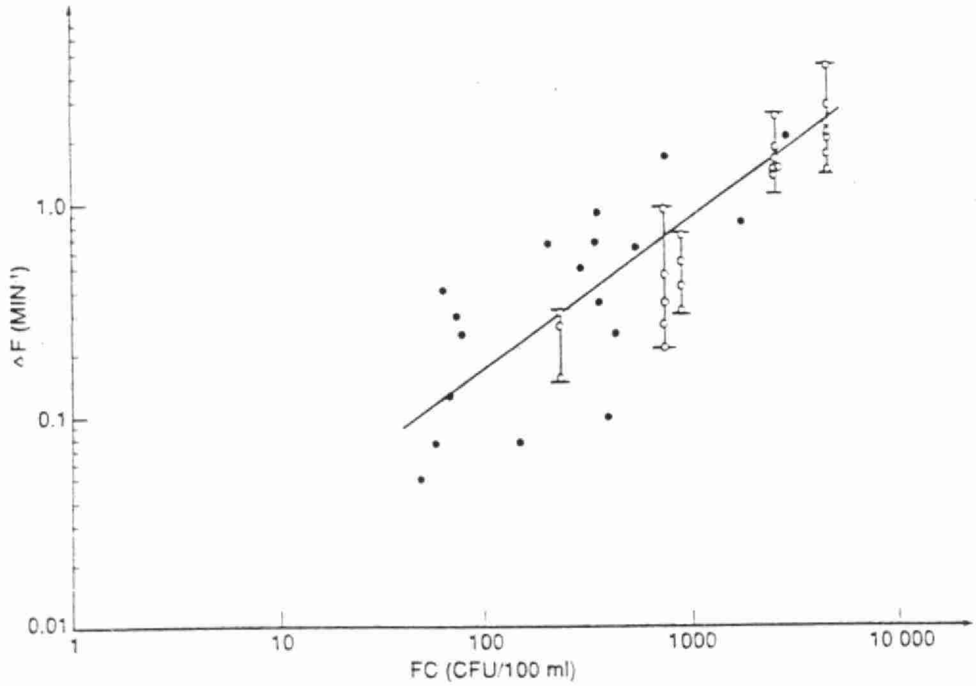


Figure 3. Initial rate of hydrolysis of 4-MU-B-D-galactoside by fecal coliform bacteria in river water. The theoretical sensitivity limit of ΔF = 0.02/min is determined by autohydrolysis of the substrate in a sterile sample. Enzyme assay temperature = 41.5°C.

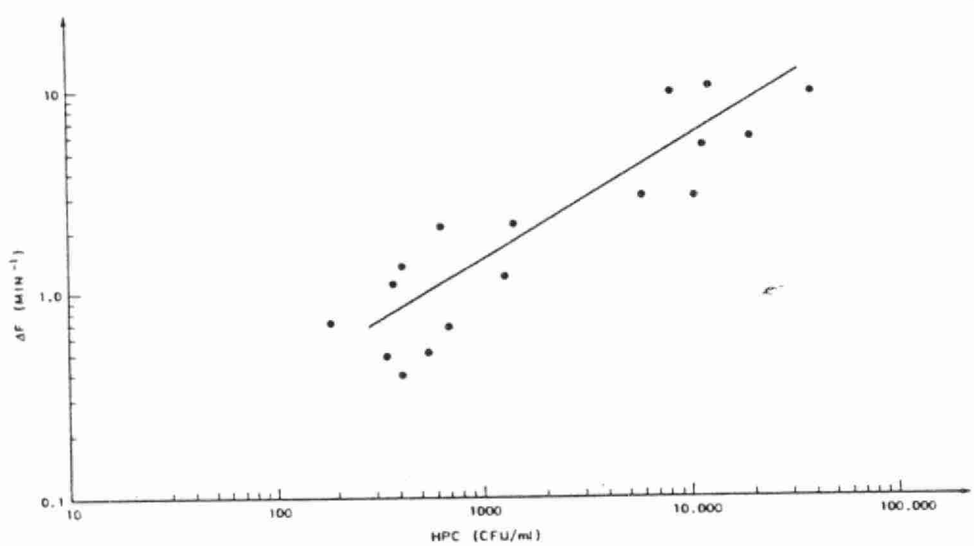


Figure 4. Initial rate of hydrolysis of 4-MU-heptanoate by heterotrophic bacteria in river water. Incubation temperature = 20.0°C.

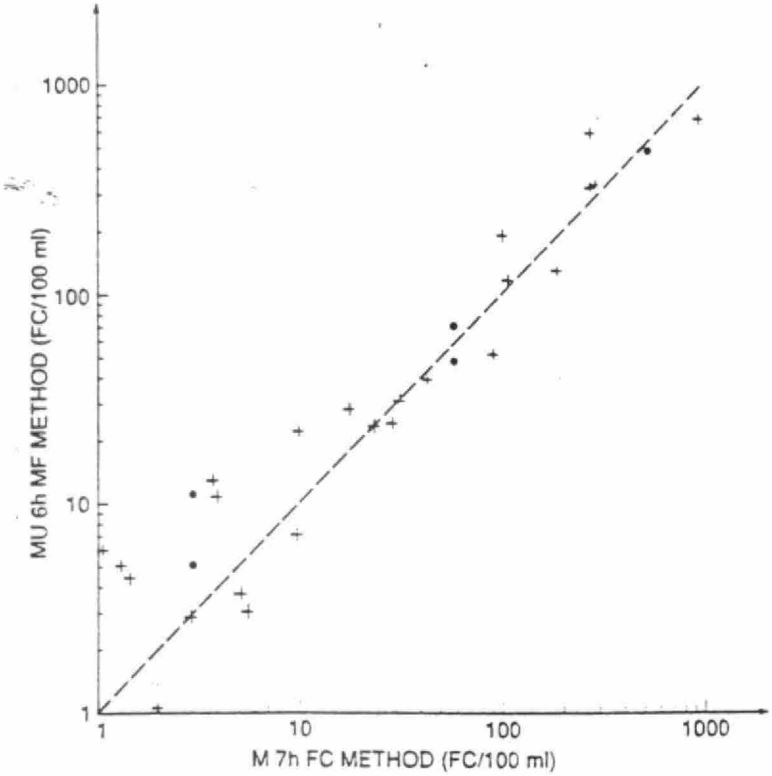


Figure 5. Comparison of FC Counts after 6h by the direct counting of fluorescing colonies (MU 6h MF) and M 7h FC Method (Standard Methods, 1985). (+) represents raw sewage-contaminated drinking water stored at 15°C and sampled after 24 to 72h for coliforms; (•) represents river water samples. Dashed line represents ideal correlation i.e., not fit to data.

PROJECT DESCRIPTION

Project Title:

An interactive, graphic information system to handle all information on water and sewage distribution systems (LEKA).

Contact (name of person, organization, address, telephone):

Østlandskonsult A/S, P.O. Box 123 N-1601 FREDRIKSTAD, Norway
Phone nr.: 47 09 314000 Telefax no.: 47 09 315579
Roy Hamre Jakobsen, Geir Bakke Nielsen,
Hans E. Magnussen

Project Description (Please attach a schematic diagram if appropriate):

General.
LEKA is an interactiv, graphic information system, specially designed to handle information about piped water and sewage distribution systems.

System functions.
Digitizing of maps. Communication with several land surveying packages. Interactiv graphical and alphanumerical input. Batch input. Interactive construction of manholes and chambers. Registration of events and production of reports/ statistics. Production of maps. Production of drawings of manholes and chambers. Production of userspecified alphanumerical reports.
Summing up, LEKA is a very usefull tool for complete management of water distribution systems.

Graphical.
LEKA is map and scale independent, data for the entire network are stored in one database in 1:1. Graphical data are stored with an accuracy of 14 digits.
The system is completely menu driven (menu on tablet). Fast and flexible zooming is handled by the workstation.

Data management.
The datastructure is handled by the network database VBAS100. The database handles the topology of the piped system in such a way that the pipes, pumps, valves etc. which are physically interconnected, are logically interconnected in the database. Graphical and alphanumerical data are stored in the database related to one physical object in the piped system.

User friendlines.
LEKA is menu driven and self explainatory. The system is very easy to use and requires a minimum of training before it can be fully operated.

Data retrieval.
LEKA's flexible report generator produces user specified reports from the database. Maps can be generated scale independent and with specified content. The system has an integrated module for interactiv construction of manholes and chambers. This module includes an extensive library of pipe parts. Events on the piped system can be logged and reported graphically as well as alphanumerically.

Operating and cost data (including data on efficiency, results, etc.):

The program is written in standard FORTRAN 77 and uses a specially designed network databased called VBAS100 for handling of both graphical and alphanumerical data. The database is designed to serve a multiuser environment.

LEKA is developed on a Prime computer, but is converted to run on ND-500 and ND-5000 computers, and uses Tektronix 4111/4207 (or similar) with tablet as graphic workstations. For pure alphanumerical input/output a standard alphanumerical terminal can be used. Batch input is now done using a special LEKA-format, this format can, however, easily be changed. Drivers for a number of plotters and digitizers are available.

LEKA has a modular structure, and is prized from NOK 100,000,- to NOK 400,000,-.

Place(s) of installation/application (including dates):

In 1986 the first version of LEKA, for administration and maintenance of electric cables, was installed at Fredrikstad elverk. Since then the "electric" version and the water and sewage version have been installed i.a. at Haugesund elverk, Sandnes elektrisitetsverk, the City of Fredrikstad, Levanger Community, Bærum Community and Karmøy Community. Installations in 1988 are planned in the following cities; Haugesund, Kristiansand, Narvik, Notodden, Sandnes, Stavanger and Trondheim, and in the counties of Onsøy, Time, Tune and Tysvær.

Patent staus, if applicable:

Owner rights belong to the consulting engineering company ØSTLANDSKONSULT A/S.

Other information (e.g., funding source, cooperating agencies, etc.):

LEKA has been developed by the owner ØSTLANDSKONSULT A.S. and is furnished by same. It has been integrated with a comprehensive digital basic mapping system, PUMATEC, partly owned by NORSK DATA.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

EMERGING WATER SUPPLY TECHNOLOGY AWWARF Code #: SC-06

PROJECT DESCRIPTION

Project Title:

Underground Denitrification NITREDOX
Denitrifikationsanlage Brunnenfeld 1 - Bisamberg

Contact (name of person, organization, address, telephone):

Rudolf Martinell, VYRMETODER AB, Nusbydalsvagen 13, 18331 Täby, Schweden

Dipl.Ing. Gerhard Jechlinger, NÖSIWAG A-2344 Maria Enzersdorf, Südstadtzentrum 4; Telefon: 02236-84601-0

Project Description (Please attach a schematic diagram if appropriate):

Full text of the description is attached together with diagrams of installation and description of the experience at the first time of performance.

Short description: .

The installation consists of two rings of recharge wells surrounding one extraction well in the centre. The outer ring serves for injection of water containing a dosage of alcohol to produce reduced conditions for denitrification in that groundwater area between the outer and inner ring of recharge wells. The inner ring of wells is used for the recharge of extracted water saturated with oxygen. So in the inner area towards the extraction well the groundwater can be post-treated under oxydising conditions so that the extracted water still contains enough oxygen to go directly into the distribution system.

Operating and cost data (including data on efficiency, results, etc.):

do not yet exist

Place(s) of installation/application (including dates):

NÖSIWAG, Pumping Station in Bisamberg is at the moment the only place of installation.

Patent staus, if applicable: Patent in Sweden 8 400 190-8, Patent for Europe 0 154 105, for Austria, Switzerland, FRG, Netherlands, Liechtenstein, France, Belgium, GB, Italy, PCT Applies SE 84/00432, Australia, Finland, Japan, Hungary, USA. National Applications: Canada 470 331, Jugoslavia P-2142/84, Spain 53 95 81 and others.

Other information (e.g., funding source, cooperating agencies, etc.):

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

Project - Description

1. Description of the underground denitrification systems of the BISAMBERG Pumping Station

The denitrification became necessary because of the increasing contamination of the well water with nitrate. Fig. 1 shows the mean concentration during the years and the trend of the concentration. The responsible engineers decided to do something in time before the nitrate content might reach the threshold value of the ÖNORM M6250 (1986) of 100 mg/l nitrate or better keep it below its recommended guideline of 50 mg/l which is corresponding to the EC (1980) threshold value or the WHO guideline for drinking water (1984).

The NÖSIWAG - engineers had already successful experiences with underground treatment of drinking water to eliminate iron and manganese according to the VIREDOX-system in the pumping station at DRÖSING. There the treatment is working already since 1982, delivering 30 - 60 l/s (108 m^3/n) of treated water at low costs of about 0,60 AS/m^3 (JECHLINGER et al. 1984, 1986).

So the VYRMETODER from SWEDEN offered a new system of reduction and oxidation for the underground treatment of the water before extraction from the well, and the first pilot system in technical size was installed at well 1 in BISAMBERG in 1987.

For the pumping station of BISAMBERG the NÖSIWAG has permission to pump nearly 23 000 m^3/d, and its delivery is about 18 000 m^3/d in summer and 8 000 m^3/d in winter out of the four wells.

So the extraction from well 1 is about 8 000 to 4 500 m^3/d and up to 65 l/s (240 m^3/h).

Fig. 2 shows the plan of the BISAMBERG pumping station with the four wells close to each other. It seems quite strange that the nitrate content in the water from the wells is rather differing as can be seen from fig. 3. It shows that in 1981 well 1 had reached 78 mg/l nitrate. That is above the limit of 70 mg/l for newly installed pumping stations according to the decree of the Minister of Health in 1984.

Because of the good results with the underground oxidation system in DRÖSING the NÖSIWAG decided to try the offered underground denitrification system of Nitredox of the Swedish firm VYRMETODER instead of other biological denitrification systems.

The system can be seen in fig. 4 which shows the supply well in the center and two circles of treatment bore holes injection. In each of these bore holes a small pump is installed. The outer ring of bore holes serves for injection of reducing organic substances. In BISAMBERG at the moment ethylated spirit is in use, in the inner ring water saturated with oxygen is injected. The area between the two circles is working as a reduction zone. The nitrate is reduced by heterotrophic bacteria and nitrate as well. The inner zone between the inner circle of bore holes and the supply well is working as oxidising reactor. Because of anisotrophy and inhomogenity in the aquifer the in situ process has to be controlled individually in each sector around the supply well. The redox potential is observed in special inspection wells situated outside the outer reduction circle between the two rings, that is in the reduced area and also in the inner oxidised area between the inner ring and the supply well. The redox electrodes allow a fully automatic guidance of the system. Fig. 5 gives an impression of this system.

The data collected from the inspection wells are regulating

the dosage of the alcohol in the outer part of the system to the outer injection wells which are supplied, with water from the two adjoining injection wells nearby.

This extraction of water and the injection of water with a dosage of alcohol is done alternatively in the wells in sectors of the outer ring system.

In the same way the oxidised area is controlled by the redox electrodes in the bore holes of the inner oxidising area. There again water is extracted from two the injection wells, saturated with air in an oxygenator under pressure. The surplus oxygen and other gases - mainly nitrogen - is degased from the water in the aeration tank. The degased water is injected into an injection well between the extraction wells. This is also done in changing sectors of the inner ring. So the oxidised area is built up around the supply well, and only water with reduced nitrate and sufficient oxygen content should get extracted from this well.

2. Experiences with a pilot installation

In BISAMBERG there are just first experiences with this denitrification system. It was started in June 1987. Figure 6 shows that the nitrate content in the supply well and also in the observation wells came down to very low values especially taking into account that the nitrate concentration in the observation well which is not influenced by the treatment system is going up in the same time. The dosage of alcohol was at that time about g/l injected water. Well 1 was delivering its water already into the supply system at that time when there were complaints arising because of bad taste of the water. The water tested muddy. The biologist found some bacteria of very small size which were already discerned in biological deironing systems. They were very difficult to perceive and were called pin points.

Maybe because of a too fast increase of the dosage of alcohol an eutrophication of the whole system was the result. Another reason could have been that the oxidation was not sufficient and that a break through of not sufficiently oxidised water was the cause of the troubles.

The TOC for the estimation of organic matter did not show any significant change, and the bacteriological control of the system according to common standards did not show an increase of bacteria.

When the dosage of alcohol into the system was stopped, the nitrate content in the inspection wells rose, as can be seen from figure 7.

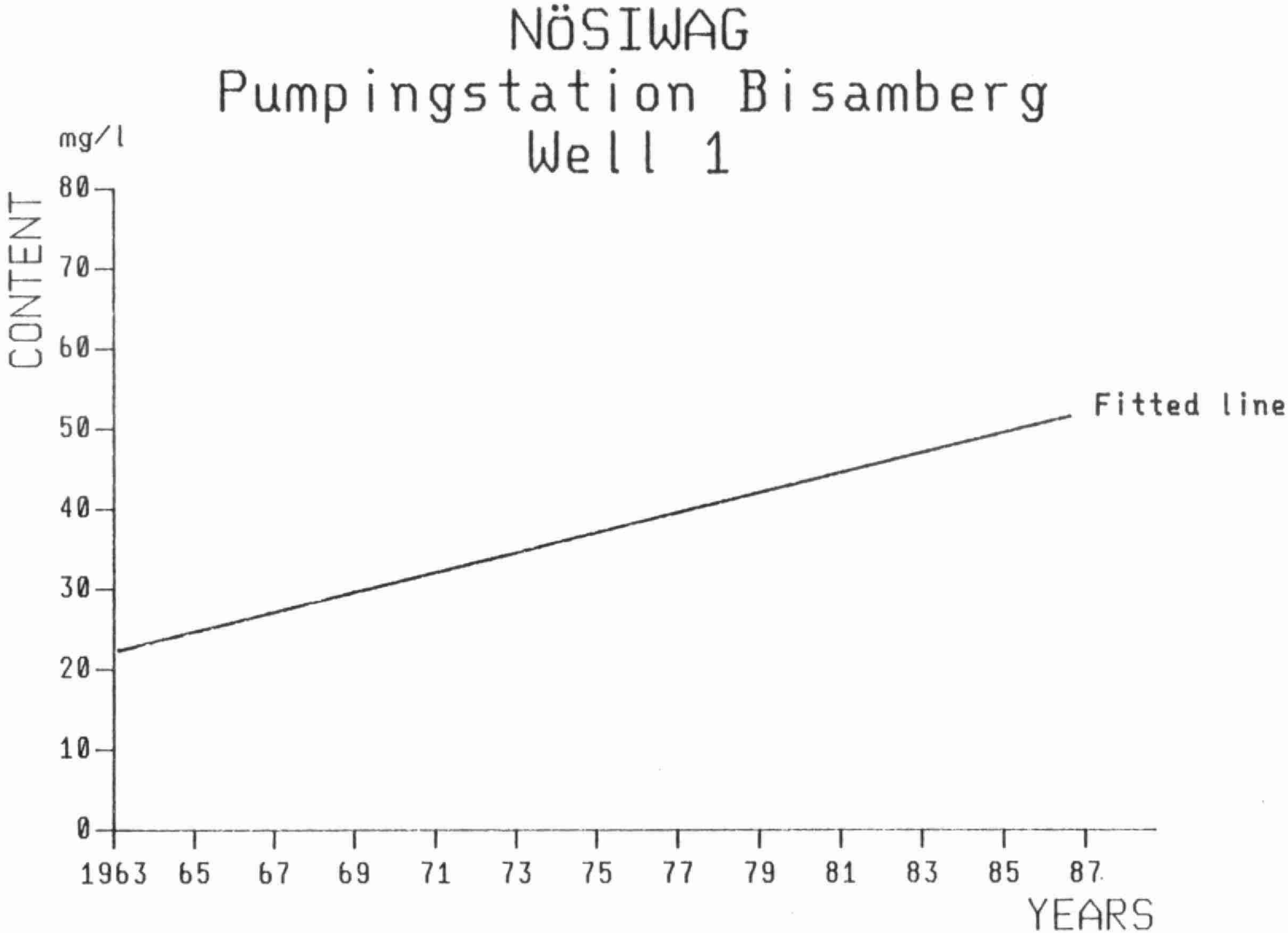
So the nitrate concentration was kept down in the supply well at about 50 % of the content in the not influenced ground water. Now the dosage is increased slowly to find the optimum value for the running of the system.

The delivering of water into the distribution system of the water supply was stopped when complaints about bad taste had started. Now the station is working just us a pilot system and the water is pumped into the canal.

I hope it will be possible at the meeting to present more experience about optimising the treatment system.

Apart from the nitrate problem in the pumping station there might arise other problems from the increasing chlorid content as can be seen from figure 8.

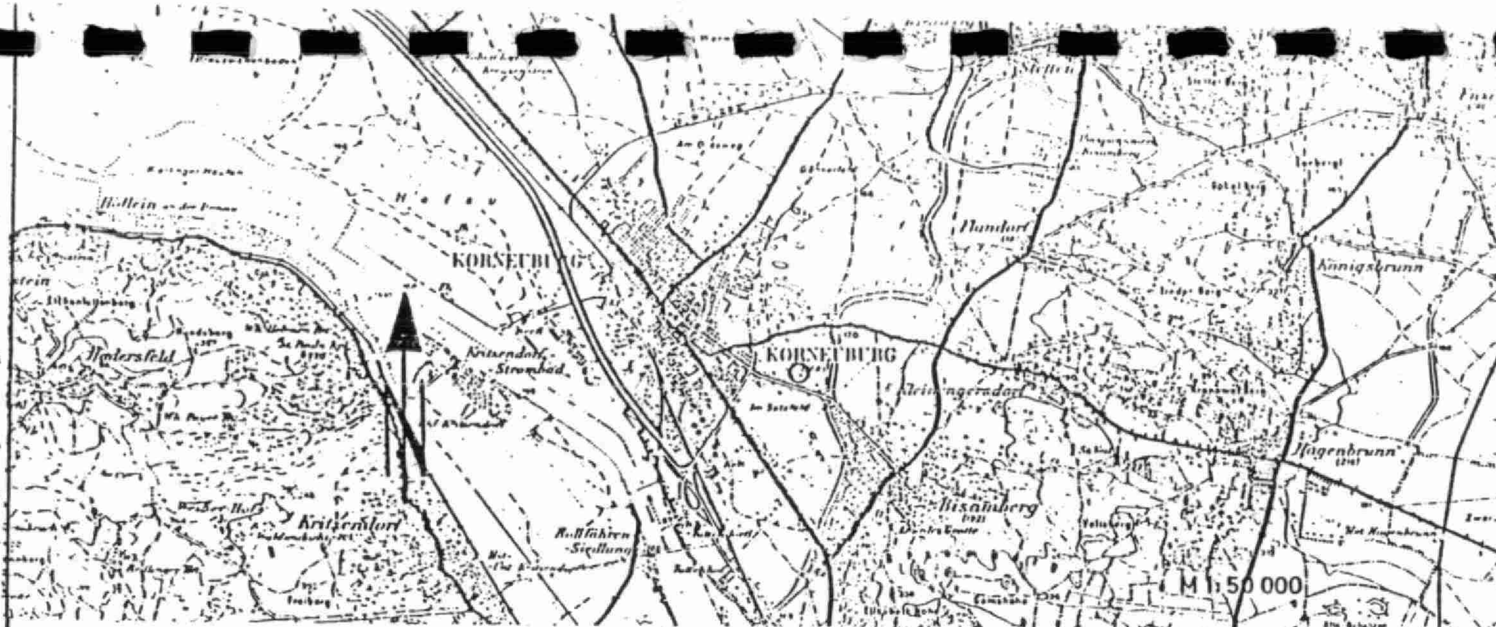
Figures



NÖSIWAG
Pumpingstation Bisamberg
Well 1
mg/l
CONTENT
80
70
60
50
40
30
20
10
0
Fitted line
1963
65
67
69
71
73
75
77
79
81
83
85
87
YEARS

SC-18

SC-19



KG: Bis[redacted]rg
pol. Gem.: Bisamberg
BH: Korneuburg
Ger. Bez.: Korneuburg

Fläche: 93.864 m²
Eigentümer: Land NÖ
Bescheid: III/1-10.152/20-1968

WVA "RUSSBACHTAL"
M 1:2880

BRUNNENSCHUTZGEBIET
BISAMBERG I

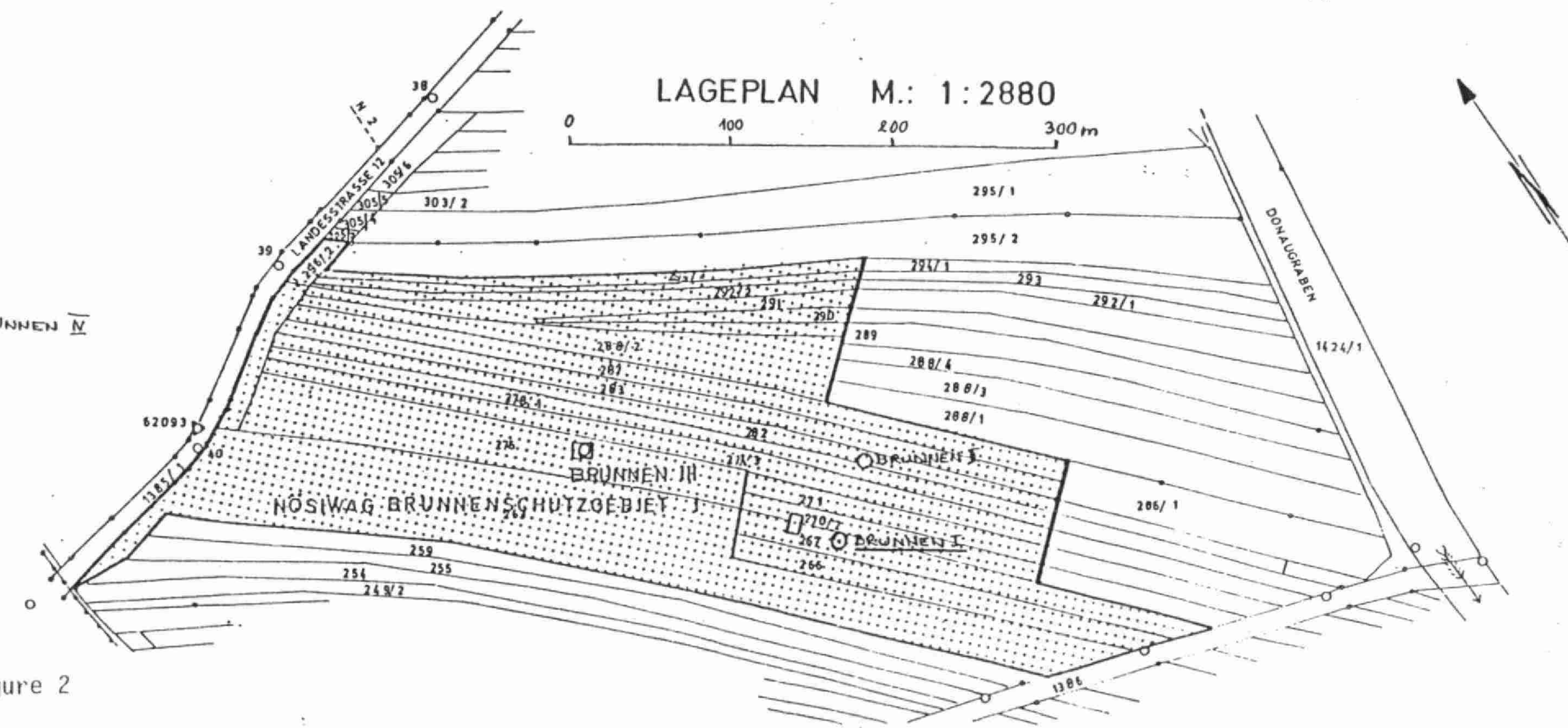
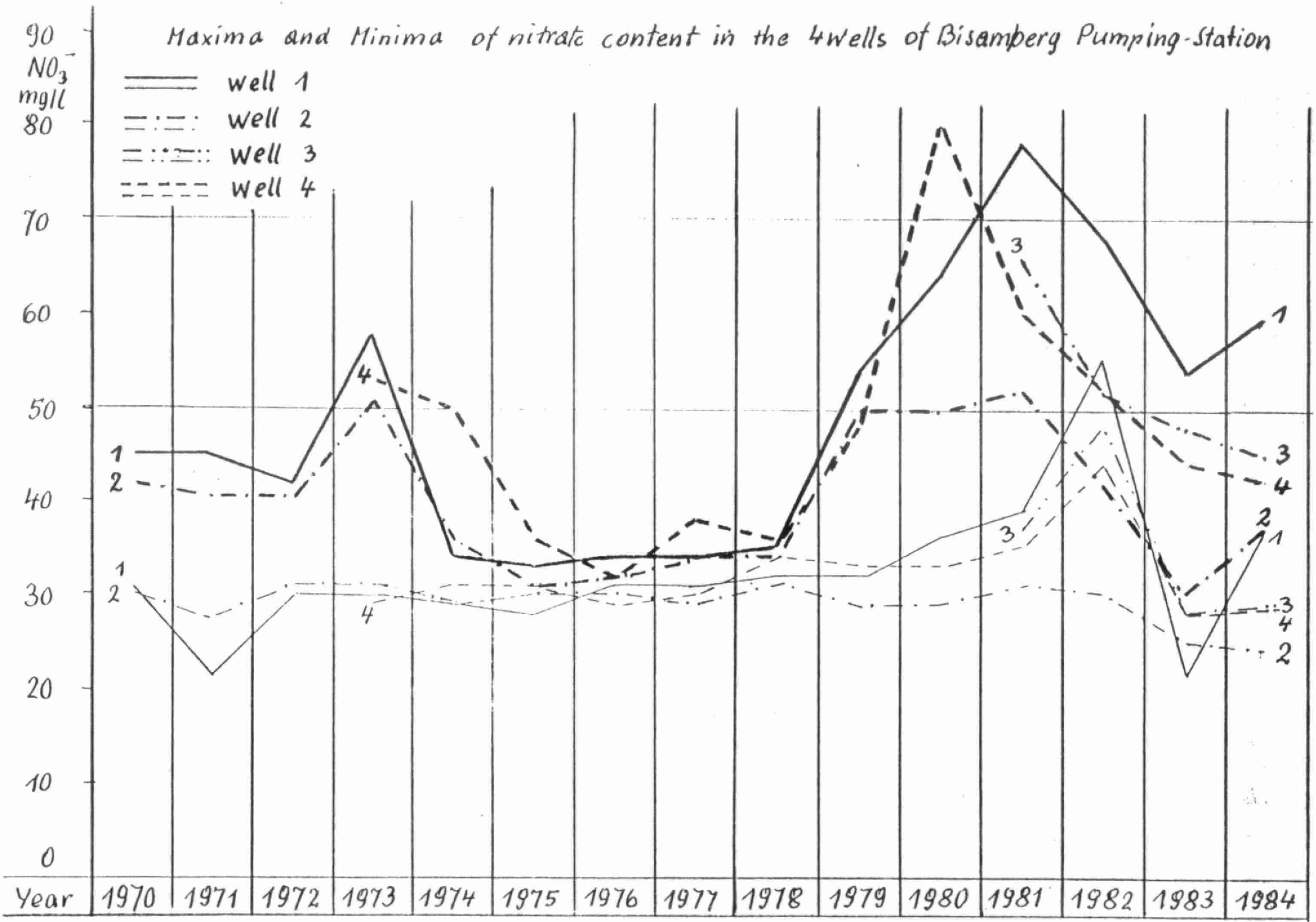
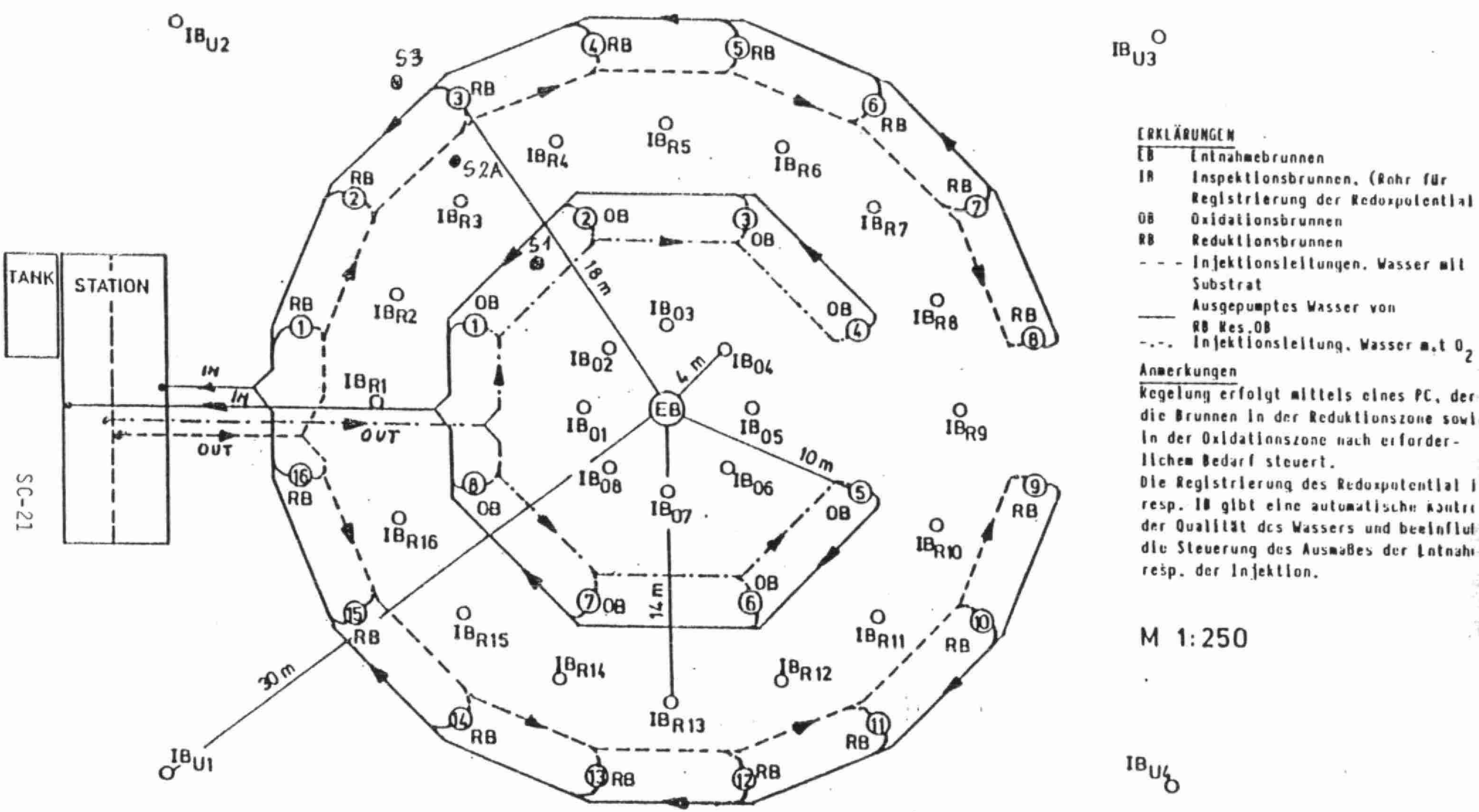


Figure 2



SC-20

Figure 3



SC-21

Figure 4

Denitrifikationsanlage Bisamberg

S 3A

NÖSIWAG
MA.ENZERSDORF, im AUGUST 1987

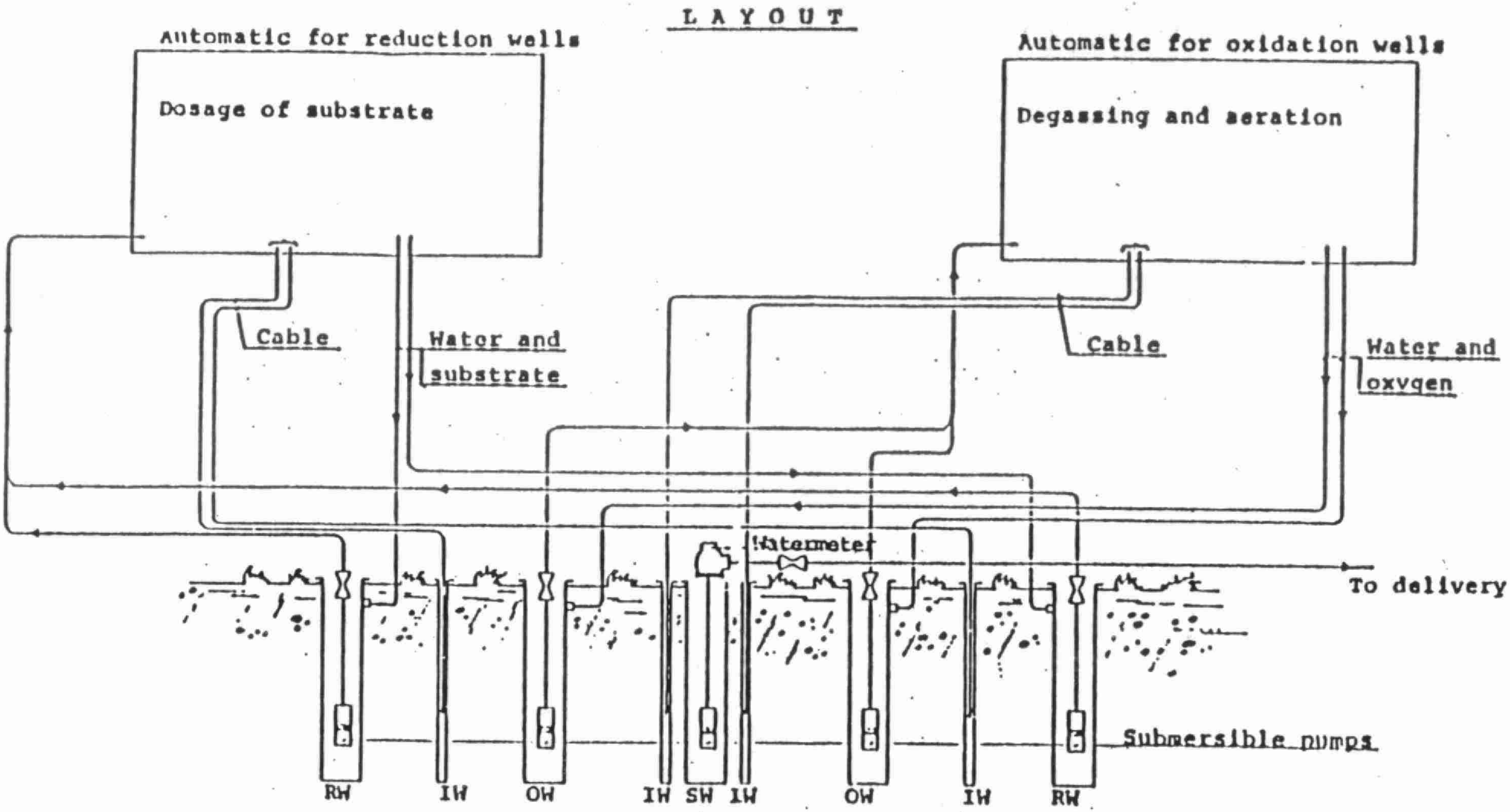


Figure 5

RW Reduction well

IW Inspection well for registration of Redox

OW Oxidation well

SW Supply well

SC-23

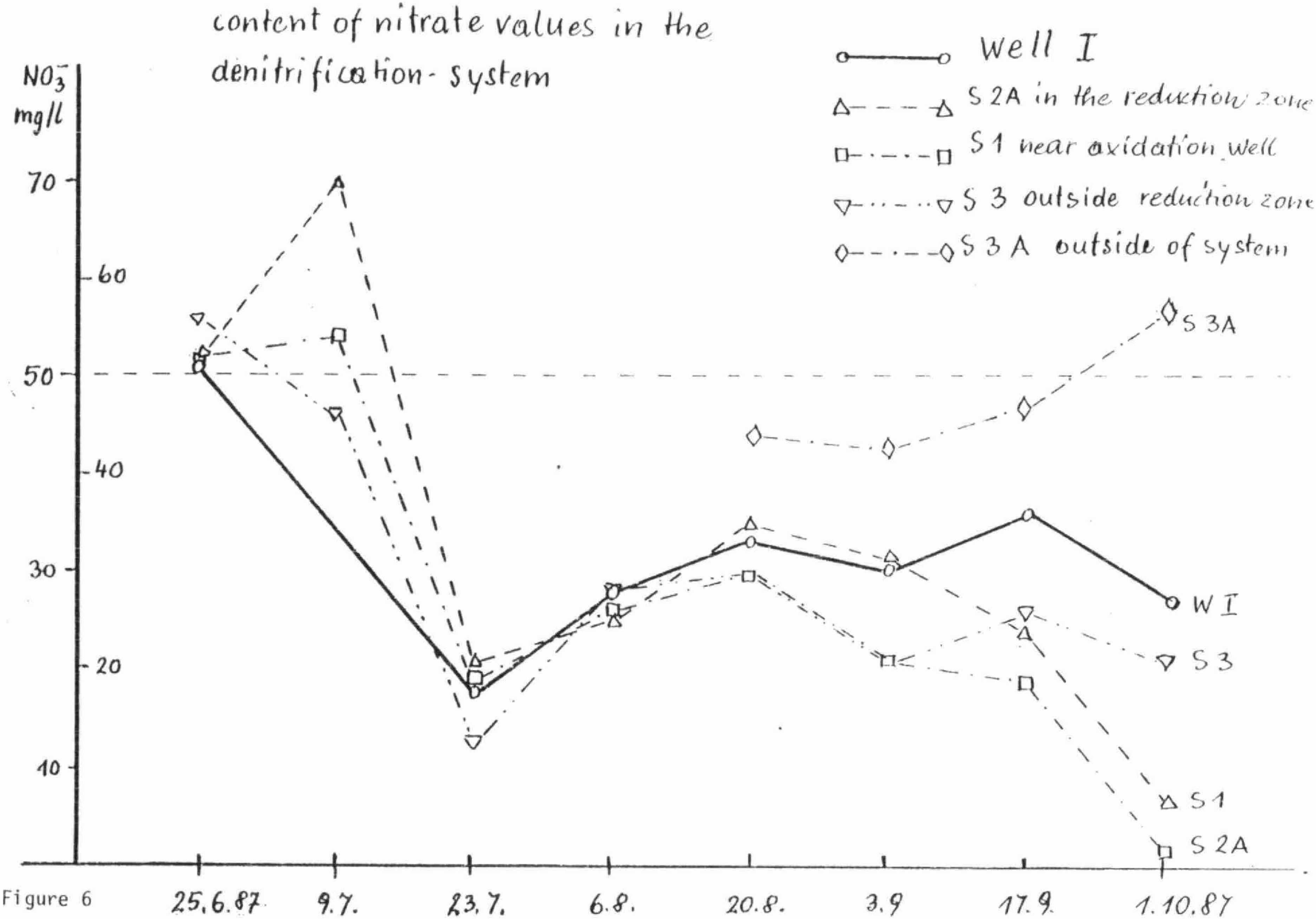
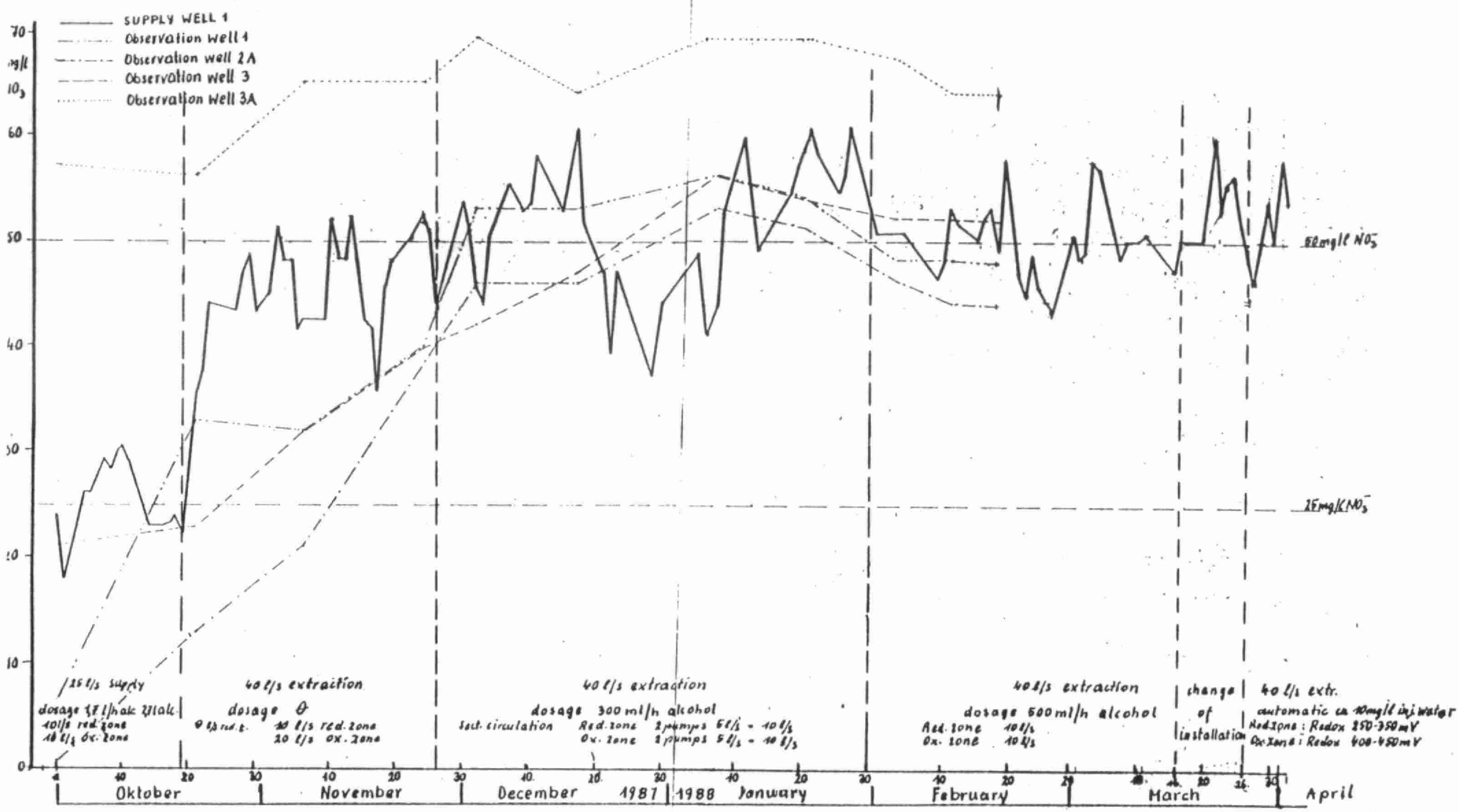
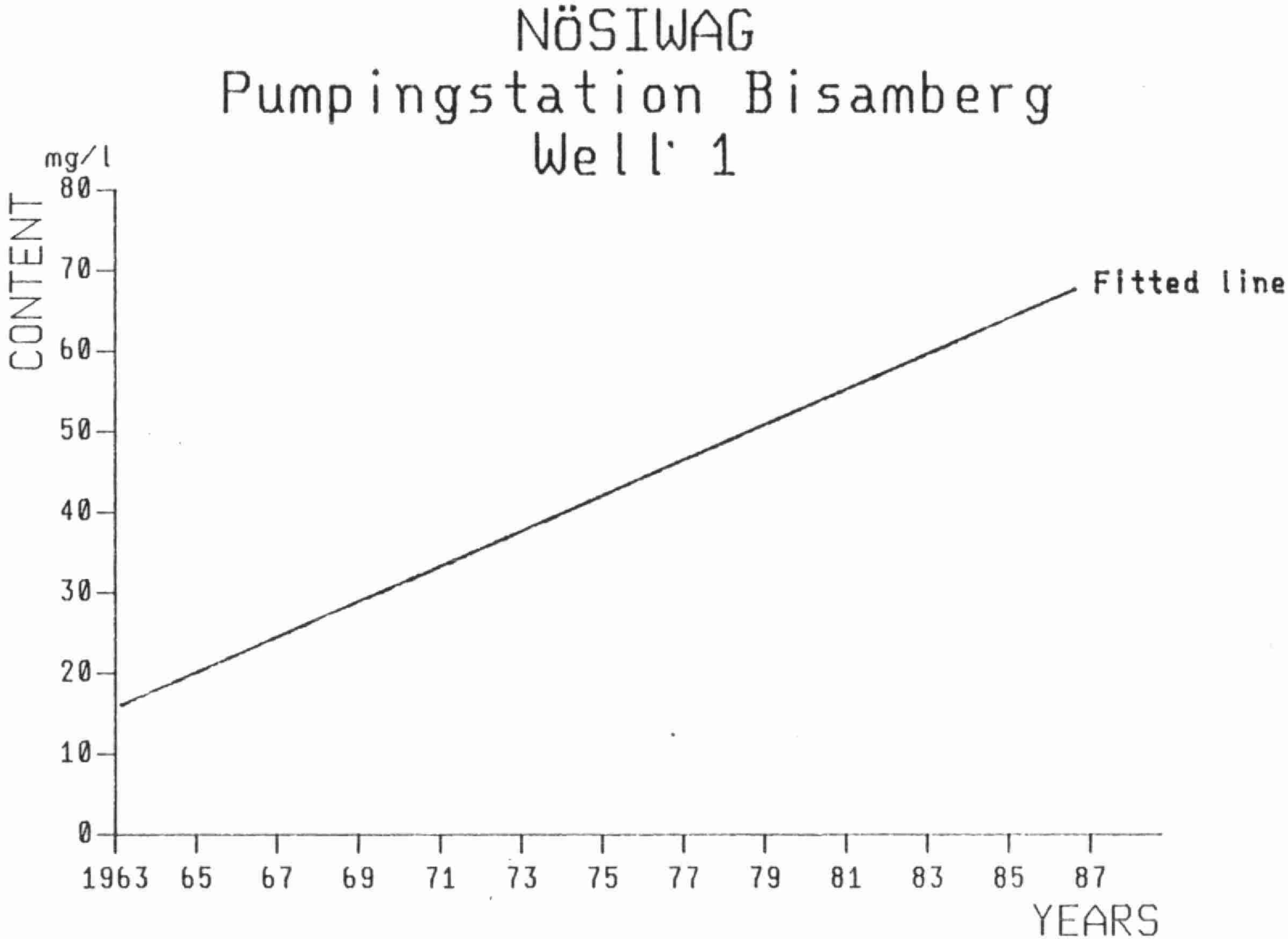


Figure 6

Figure 7
Course of nitrate-content in the underground treatment system



SC-24


NÖSIWAG
Pumpingstation Bisamberg
Well 1
mg/l
CONTENT
80
70
60
50
40
30
20
10
0
Fitted line
1963
65
67
69
71
73
75
77
79
81
83
85
87
YEARS

SC-25

THE VYREDOX AND NITREDOX METHOD

IN SITU TREATMENT OF GROUNDWATER

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ABSTRACT

Nearly one fifth of all water used in the world is obtained from groundwater. The protection of water has become a high priority goal. During the last decades pollution of water has become more and more severe. Today groundwater is more and more used in comparison with surface water. Recently we have seen accidents, which can pollute nearly all surface water very quickly. Generally the groundwater is easier to protect, as well as cheaper to purify, and above all it is of better quality than the surface water.

The traditional method to treat the water in filter has during the past two decades got alternatives and that is in situ water treatment i.e. the **VYREDOX** and **NITREDOX** methods.

The most common problem regarding groundwater is too high content of iron and manganese, which can be reduced with the **VYREDOX** method. In some areas today there are severe problems with pollution of hydrocarbon and nitrate as well, and with moderating of the **VYREDOX** treatment method it is used for hydrocarbon and nitrate treatment as well. The method to reduce the nitrate and nitrite is known as the NITREDOX method.

VYREDOX

Next only to oxygen, silicon and aluminum, iron is the fourth most abundant element in the earth's crust. The crust consists of iron to 4,7 per cent by weight. Expressed as oxides, there are 3,7 per cent ferrous oxides (FeO) and 3,1 per cent ferric (Fe_2O_3) in the crustal rocks, that is divalent and trivalent iron occur in approximately equal amounts. Manganese is abundant in the earth's crust to about 0,10 per cent by weight. In ground water the iron content usually exceeds the manganese content even though manganese is much more soluble in natural waters. The iron content often exceeds that of manganese with a factor ten or more.

Iron and manganese in the water cause troubles to the user in many ways. Therefore it is necessary to decrease a high content of these metals before the water is made use of.

With a controlled water treatment in the soil many of the disadvantages related to a traditional waterworks can be avoided. The **VYREDOX** method tries to achieve this by adapting the natural processes of ground water purification to the environment of the supply well.

Iron occurs in two states of oxidation in nature, divalent (Fe^{++}) and trivalent (Fe^{+++}). The divalent form is likely to stay in solution in a natural ground water, whereas the trivalent will be precipitated, for instance as an oxide (Fe_2O_3) or an oxihydroxide ($FeOOH$). The state of oxidation is depending much on the amount of dissolved oxygen in the water. Hence it is normal that the amounts of dissolved iron and manganese are low in such aquifers where aerated rain water can seep rapidly into the ground water.

In some areas, however, some layer in the soil above the aquifer has a low permeability, and the percolation of aerated water into the aquifer may be decreased substantially or even entirely prohibited. If this occurs, the iron and manganese content in the water will rise. The **VYREDOX** idea is to compensate for the lack of oxygen in such ground water, and thus to turn the balance of the chemical system in the aquifer over to the oxidative side. Then the natural purifying processes will be allowed to operate again, and the water will become free of iron and manganese.

Figure 1 illustrates how the arrangement of a typical **VYREDOX** I plant can look like. The working principle is quite simple: The wells are treatened one at a time as the content of iron and manganese tends to rise. The oxygen is simply taken from the air and dissolved in the injection water. This in turn originates from another **VYREDOX** treated well in the aquifer (or from a water reservoir). To ensure a sufficient distribution of the injected, aerated water certain injection wells are drilled around the supply well.

As the oxygen-enriched water is injected into the aquifer an oxidized zone is established around the well. This will stimulate the activity of certain iron and manganese bacteria which occur in natural waters. These bacteria are of different kinds, and they do not form a systematic group. Normally the organisms belong to the species Leptotkrix (Sphaerotilus discophorous) or Gallionella ferruginea. They often occur together with precipitates of iron and manganese in ground water aquifers.

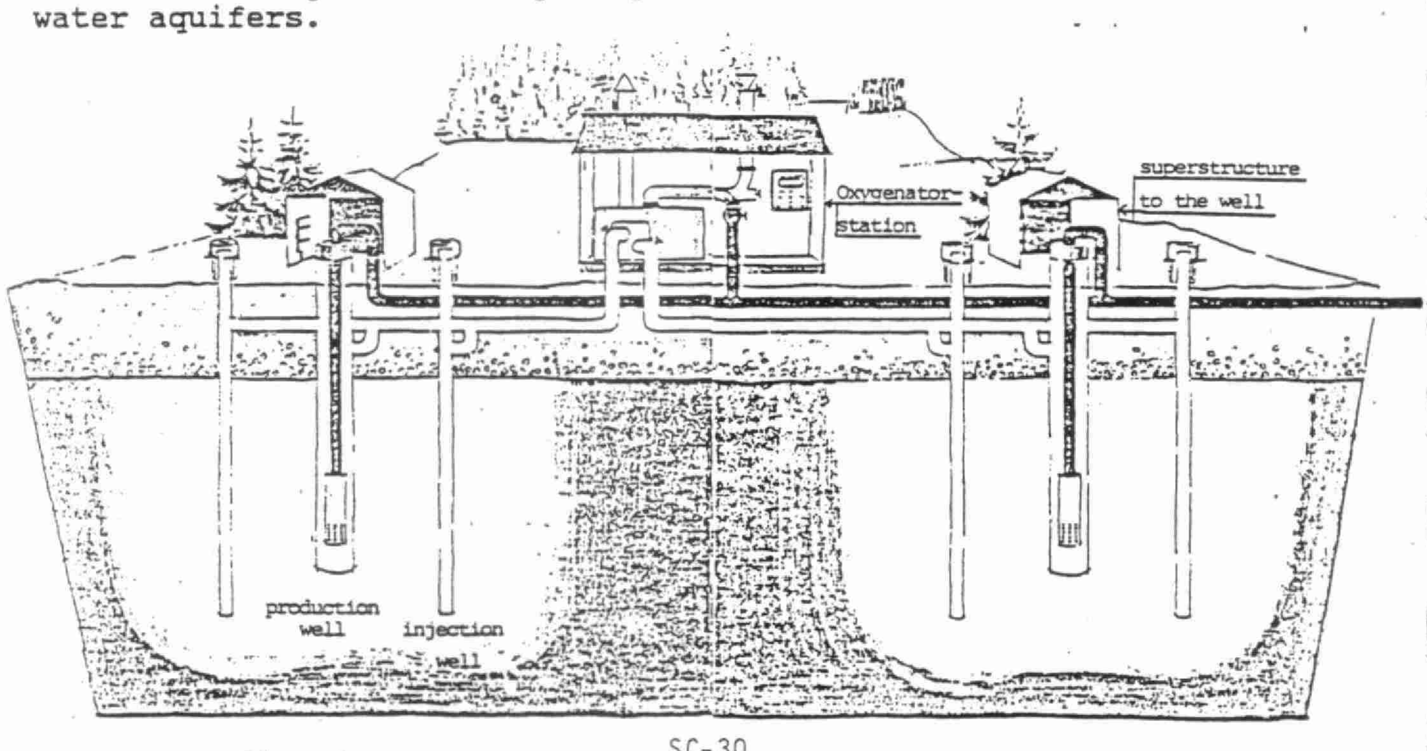

Fig. 1

Schematic outline of a VYREDOX waterwork. The plant consists of two supply wells. The ground water is pumped directly out to the mains from the supply wells. If the iron content begins to rise in one of the wells is pumped to the oxygenator from the other supply well. Here, oxygen is entranced from the air, and in the aeration tank excessive oxygen and other gases are released. The oxygen-enriched water is then pumped down into the aquifer through the injection wells surrounding the other supply well. This goes on for about 20 hours.

Around a ground water well that have been treated with injected, degassed and oxygenated water an oxidized zone is built up. At the border of the oxygenated part of the aquifer a redox gradient is established. The bacterial activity in this region is stimulated, and an iron and manganese precipitation zone is developed. When the well is pumped, the ground water will be filtrated through this zone. This is illustrated in figure 2. As the water reaches the well it will be free of iron and mangenese. If the pumping is continued, the precipitation will take place closer to the well. Finally, the iron and manganese contents will begin to rise again. The injection with oxygenated water is then repeated. As a result, the moving redox gradient will distribute the iron and manganese concretions throughout the oxygenated zone around the well.

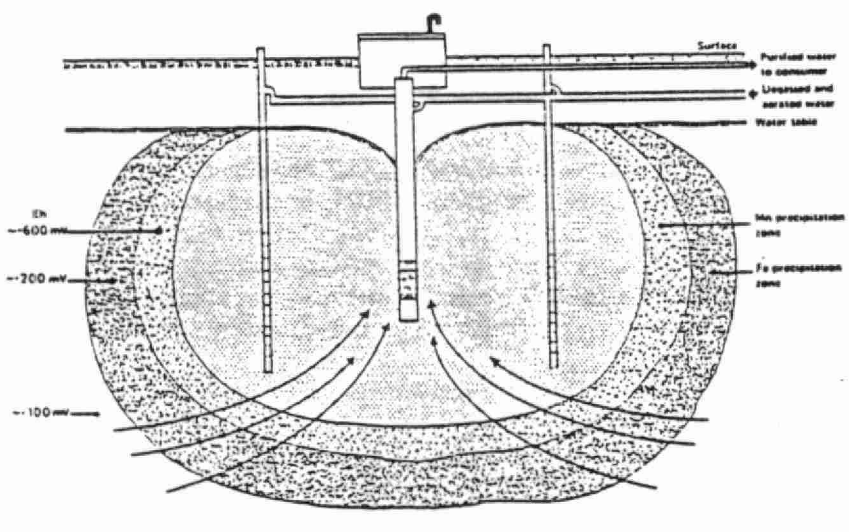

Fig. 2.

With the VYREDOX method an iron and manganese precipitation zone is achieved around the supply well. If the well is pumped, the ground water will pass through the zone, and the iron and manganese will be retained in the soil. Iron is precipitated before manganese because of the "shape" of the redox-potential. Only water free of iron and manganese will enter the supply well.

To the left in figure 2 some redox potential values (Eh) are indicated. They are typical for an aquifer with a pH-value close to 7. Moving towards the well with a redox electrode, a drastic increase of the redox potential with several hundred millivolts will be observed as the precipitation zone is passed.

The absolute value of the redox potential in a certain aquifer depends on many environment properties. In a reduced water with a low pH the redox potential will show a low value, perhaps below zero. Such water is likely to contain large amounts of methan and hydrogen sulphide, dissolved iron and manganese. In order to oxidize the metals, especially the manganese, a very high value of the redox potential is required. Thus the redox potential in such cases has to be greatly increased, maybe with a thousand millivolt or so.

This demonstrates a limitation of the method: If the pH of the ground water is very low, it will be difficult to establish the redox potential which is required for a sufficiant manganese oxidation. Generally, it is easier to remove the iron, and the lower the pH-value is, the more often the aquifer has to be oxygenated.

The influence of pH and the redox potential may be illustrated in a diagramme with equilibra between different oxidation transitions. This is done in figure 3, where the two sloping lines indicate equilibrum between the transitions $Fe^{++}/Fe(OH)_3$ and Mn^{++}/MnO_2. If the redox potential is increased at a constant pH-value the dissolved iron will be oxidized and precipitated before the manganese.

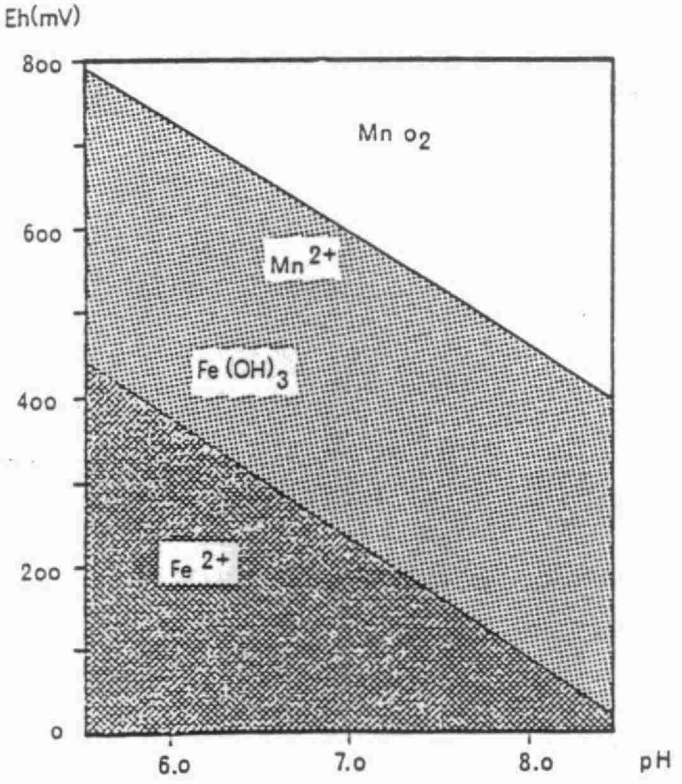

Fig. 3

Dissolved iron (Fe^{++}) and manganese (Mn^{++}) and the precipitated variants iron-hydroxide ($Fe(OH)_3$) and manganese-dioxide (MnO_2) as functions of pH and redox-potential Eh. The sloping lines indicate equilibrum, and they are not absolute fixed. As the redox-potential is increased for a given pH-value, first iron and then manganese will be precipitated.

Once the VYREDOX process has been started up, more and more compounds of oxidized iron and manganese will be precipitated in the aquifer. This will increase the rate of adsorption of divalent iron and manganese on the surface of the precipitates. Thus the oxidation process will take place in two steps, first adsorption and then oxidation. In the pH range of natural ground waters the hydrous oxides FeOOH and MnO_2 seem to play important roles in the sorption of divalent iron and manganese. The adsorption process also takes place on the bacteria stalk surface.

The precipitation zone has to be properly developed in order to achieve a good purifying result and a high efficiency ratio. Its size and shape has to be fitted not only to the aquifer but to each singe supply well. In order to achieve this the injection wells are needed. Both the oxygenation kinetics and the precipitation kinetics have to be considered in dimensioning the zone. About one per mille of the soil's pores in the oxidation volume is allowed for the precipitation of one year.

VYREDOX I AND II

The VYREDOX method became a reality during the sixties after different kinds of testing, research and modifications. The first commercial VYREDOX plant was built in 1969. Today there are more than one hundred VYREDOX plants in more than ten countries. The majority of them are designed according to the VYREDOX I princip and some according to the VYREDOX II princip.

VYREDOX I

The VYREDOX I design is when the injection wells are used only for injections. During the injection the pump in the supply well belonging to the same well group (fig 1 and fig 2) are with some exceptions stopped. The injection goes on for 20-30 hours and after the injection there are a contact time of 4-10 hours. The injection water is taken from a supply well nearby or from a water reservoir.

The precipitation zone around a well will take some time to be built up. Often ten injection cycles or more will be required before the efficiency ratio of the plant can be determined. The efficiency ratio is defined as the ratio between the amount of pure water pumped out after an aeration and the amount of injection water used for aeration. This value varies much from plant to plant, depending on the chemical and hydrological circumstances in each case. Normally, a value of around 10 will be obtained, but the variation is as large as from about 3 to 50. There are examples where the efficiency ratio is up to more than 50.

VYREDOX II

The VYREDOX has been developed further and since VYREDOX I needs at least one extra supply well or a reservoir to have water for injection as the pump in the production well is switched off during the injection, VYREDOX I turned out to be too expensive at small well sites. As a result the VYREDOX II was developed (fig 1, 2 and 4).

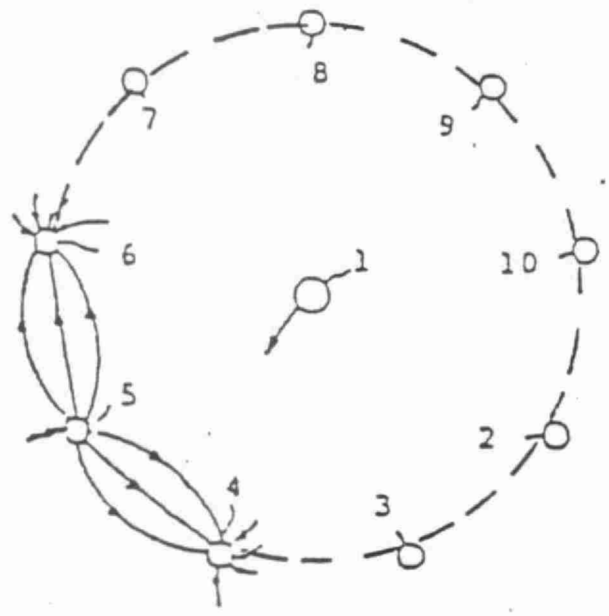

Fig. 4 1. Supply well
2-10. Injection wells on the oxidation ring

The principle is that in each injection well a submersible pump is installed and the injection pumping goes on cyclic in the injection wells independently whether the pump in the supply well is in operation or not. For example, injection wells number 1 and 3 are pumped via an oxygenerator where the water is degassed and aerated and then injected in the intermediate well number 2. After a certain time of this pumping/injection and a period of contact time, the pattern is that water is pumped from injection wells number 2 and 4 and injected into number 3 and so on. The number of these injection/pumping wells differ depending on the conditions. There are examples from 3 up to 16.

This pattern of pumping/injection creates a super-positioned hydraulic gradient to the supply well, when the supply well is in operation and a hydraulic gradient between the injection/pumping wells like a "curtain". In this oxidate zone iron and manganese will be oxidated an precipitated. For three years we have had VYREDOX II water works in operation. Today there are about 10 plants in operation.

EXPERIENCES FROM PRACTICAL APPLICATIONS

One of the first questions arising in connection with a presentation of the VYREDOX method is that of clogging. Often a fear is expressed that the aquifer soon will be clogged by precipitations, resulting in a severe decrease of the well's pumping capacity. The surprising answer is that the effect is rather the opposite! If the oxygenation zone is properly developed, and if the plant is run correctly, the pore volume of the aquifer will be affected only very slowly. Since reduced water often has proved to be responsible for well clogging, the VYREDOX treated well will be protected by the shield of oxygenated water around it. The precipitations will be located to a large pore volume at a sufficient distance from the well where no harm is done. Thus the well yield is maintained, and in some cases an increase of it has been observed during the first months of VYREDOX operation.

Much attention has been paid at the built plants to the matter of precipitation and clogging. At the oldest Swedish plant in Grimsås, built in 1971, soil samples have been taken and investigated. It is not possible to take such samples without disturbing the pore structure somewhat. However, samples with relatively undisturbed sediments have been microscopically examined. It has not been possible to identify any severe precipitation in the intersticial spaces. In the lowermost sample, at the middle of the well screen, one or a few per cent of the pore volume show precipitates. The texture of the precipitates can in some cases be interpreted as "bacterial iron stalks". Also a mineral transformation has been observed from a brownish aggregate into reddish hexagonal plates. This is interpreted as a transformation from iron-oxihydroxide (e.g. goethite) into hematite. Thus the bacterially formed iron precipitates may turn into more stable minerals such as hematite. This possibility has also been indicated by laboratory experiments.

The original contents of iron and manganese in the untreated water varies much from plant to plant. Normally they lie in the intervals 0,3 - 15 mg/l iron and 0,2 - 4 mg/l manganese. In addition to the iron and manganese removal the method has proved to have some other positive effects on the water quality.

As a specific example of a VYREDOX I plant in Drösing/March (lower Austria) can be mentioned. The water works was taken in operation during the spring 1982. The geological conditions are different from those in Scandinavia, because there is a high content of limestone and dolomite in the gravel and sand, with strata of marl and clay (fig. 5).

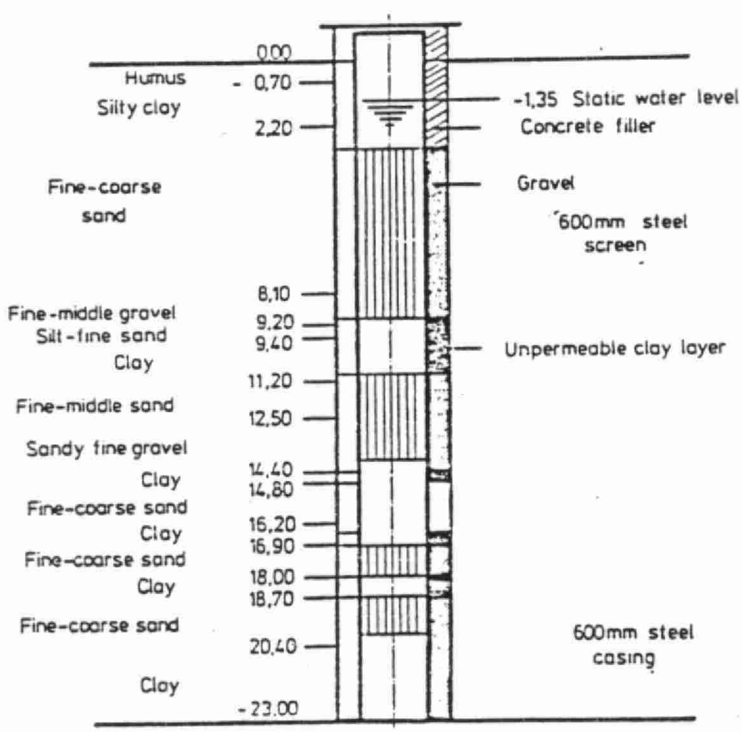

Fig. 5. Geological strata at water plant Drösing/March.

The quality of the raw water from the different wells in Drösing may be seen in Table 1.

TABLE 1 Chemical analysis of untreated ground water (mg/l)

Parameter		Well 1	Well 2	Well 3
Calcium	Ca^{++}	92	95	97
Magnesium	Mg^{++}	58	55	55
Natrium	Na^{++}	42	43	43
Potassium	K^{+}	4,3	4,6	4,2
Hydrogen carbonat	HCO_3^-	486	489	491
Chloride	Cl^{--}	38	35	33
Sulphate	SO_4^{--}	100	125	95
Nitrate	NO_3^-	<1	2,2	<1

The iron and manganese content in the well water have been confirmed by a multitude of analyses. The results are summarized in TABLE 2.

TABLE 2 Iron and manganese content of untreated water (mg/l)

Iron	min	max	average
Well 1	0,16	0,49	0,35
WELL 2	0,20	0,42	0,27
well 3	0,26	0,40	0,31
Manganese			
Well 1	0,33	0,54	0,48
Well 2	0,31	0,54	0,39
Well 3	0,25	0,39	0,32

The processing should produce water of a purity that meets the requirements of the standard valid in Austria, ÖNORM M 6250 (quality standards for drinking water) i.e. iron ≤ 0,1 mg/l calculated as Fe, and manganese ≤ 0,05 mg/l, calculated as Mn. This standard is the most common standard in several countries. It has further been stipulated that during the running of the plant a ratio of at least 4:1 between the processed water, which is piped out, and the water returned for oxygen enrichment underground must be achieved.

At the site of the plant there are numerous separated aquifers which contain water under pressure, artesian aquifer. The highest groundwater hirozon is not under pressure. It is not used to supply water and is therefore not a part of the system.

The plant should continually purify 30 l/s (108 m^2/h) of water. There are three identical supply wells, and it is possible to extract all the water from each one individually. The maximum capacity of the plant is thus 90 l/s.

The plant was built according to fig. 6. Around each of the three wells, a ring of six injection wells was built. Due to the local conditions it was necessary to separate the supply of water for the main network from the water to be passed through the oxygenator into the injection wells, i.e. two separate pumps with different pressures was built.

The oxygenator and the necessary pipes are situated in a pipe canal under the station. With three supply wells being available it is possible to use one well for the production of purified water for the main supply, and to use purified water from a second well for infiltration in the injection wells of the third well after being enriched with oxgen. After the termination of the infiltration (after 24 hours) all three wells are available for the production of purified water, as long as purified water can still be drawn from the supply well in the first injected well group. When there is no more purified water in this supply well e.g. water of acceptable quality, degassed and oxygen enriched water is infiltrated into its injection wells by means of an automatic control governed by time and capacity.

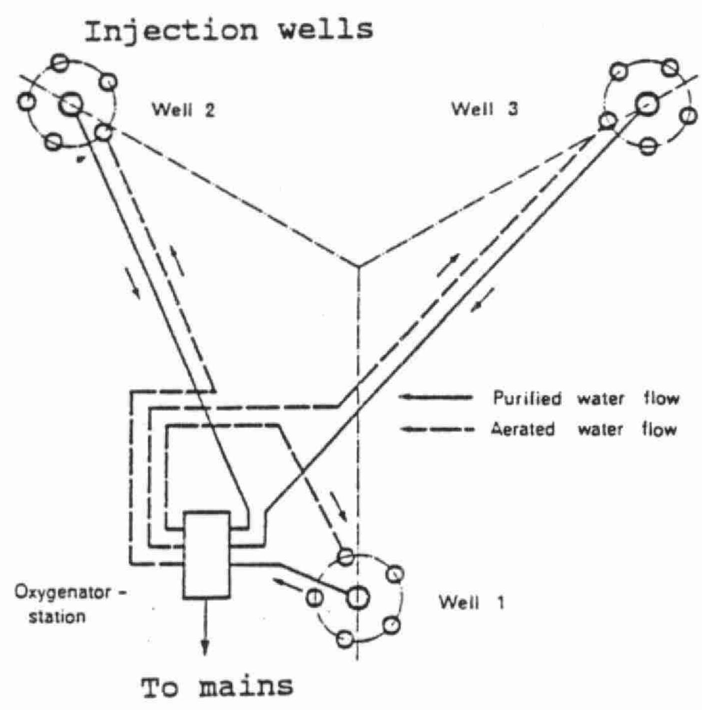

Fig. 6. Waterplant in Drösing with three supply wells complete with injection wells and the oxygenator station.

The only problem in time of construction was during the running in due artesian ground water. This fault could be corrected simply by using a mineral sealing compound.

There was intensive monitoring of the system to ascertain the concentration of iron and manganese.

The results of this monitoring are as follows (fig. 7):

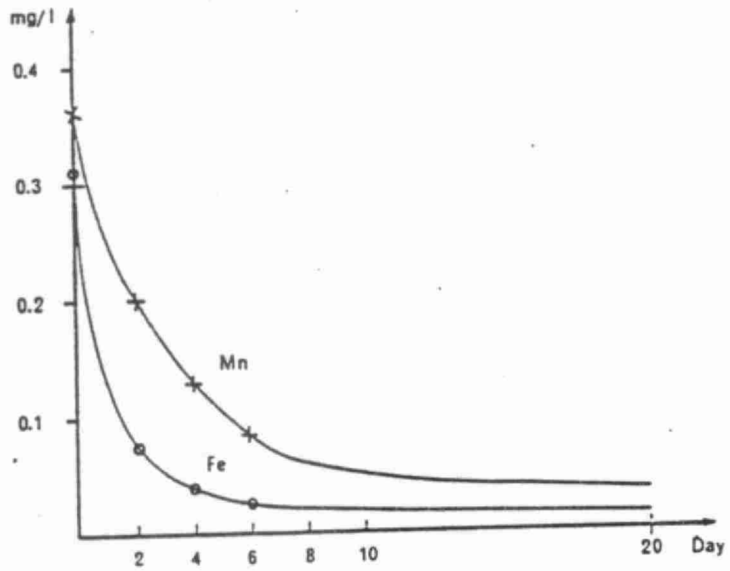

Fig. 7. Reduction of iron and manganese

The measured values of iron decreased in the shortest time to values of ≤ 0,1 mg/l, but in the majority of cases values of ≤ 0,05 mg/l, were found. The measured values of manganese, however, decreased for one month, practically without exception, to values of ≤ 0,05 mg/l, and the majority to values of ≤ 0,03 mg/l.

At the beginning of the running of the plant, the ratio between processed water delivered into the mains and the recycled, degassed and oxygen enriched water was 2:1. This ratio was increased during a few months to a value of 7:1. This value is possible to increase if necessary. Despite of this increased ratio, there were no changes in the rate of removal of iron and manganese.

The total investment costs were 4,300.000,-- A.S.(without V.A.T.). Out of this sum about 2,400.000,-- A.S. was spent on equipment. The costs of on site constructions such as injection wells, power connection and

other necessary equipment were about 1,900.000,-- A.S. The construction of more buildings was not necessary. Otherwise, an inspection of two hours per week is sufficient. As yet, there have been no operating problems.

Detailed calculations of the operating costs from May 1983 onward are available. The only operating costs are for electricity. The amount of power needed depends on the quantity of water treated and on the ratio between recycled water and that pumped into the main supply; this power demand is shown in TABLE 3.

TABLE 3. Ratio between processed and recycled water

Ratio	2:1	3:1	4:1	5:1	6:1	7:1
kWh	60.320	7.994	7.236	18.186	3.704	6.054
m^3	122.201	67.027	93.431	288.124	88.347	148.484
$kWh/1000m^3$	493,6	119,3	77,4	63,1	41,9	40,8

Within three months of operation the plant met the expectations in the removal of iron and manganese from treated water. Considering operating and investment costs, it is cost-effective. Up to now there has been no deposition in the well pipes, nor have any changes in the permeability of the aquifier been observed.

NITREDOX

Nitrate in groundwater causes several problems even if the nitrate itself is not so poisonous. The lethal dose for an adult is around 10 - 15 g. However, the nitrate can be reduced to nitrite, which is much more poisinous, especially for babies, especially up to an age of 6 months, while nitrite gives a reaction with the hemoglobine in the blood to methaemoglobinaemia. Methaemoglobinaemia cannot work as the transporter of oxygen in the body. This gives as a result blue babies. Another problem is the cancerogenic nitrisaminos, which are produced from nitrate as well as nitrite.

The drinking standard in several countries accept for nitrate 50 mg/l with a future guideline value of 25 mg/l.

DIFFERENT DENITRIFICATION METHODS

On the market today there are a few denitrification methods used.

In principle three different methods can be mentioned:

- Ion exchange
- Reversed osmos
- Biological treatment.

NITREDOX - A BIOLOGICAL TREATMENT METHOD

NITREDOX is an in situ denitrification method, which with the help of the naturally existing microorganisms, is reducing nitrate and nitrite in the water to an aceptable level. Nitrate has been reduced from more than 100 mg/l down to below 25 mg/l and nitrite to below 0.02 mg/l.

Around each supply well a number of injection wells are drilled, in principle on two rings with different radius (fig. 8). In each injection well a small pump is installed. The injection wells situated on the bigger ring are used for reduction and the injection wells situated on the smaller ring are used for oxidation in a specific running pattern. In the big reducing ring the nitrate and nitrite are reduced and in the small oxidizing ring the nitrogen gas is degassed and an eventual rest-content of nitrite is oxidized as well as iron and manganese are oxidized and precipitated in the ground.

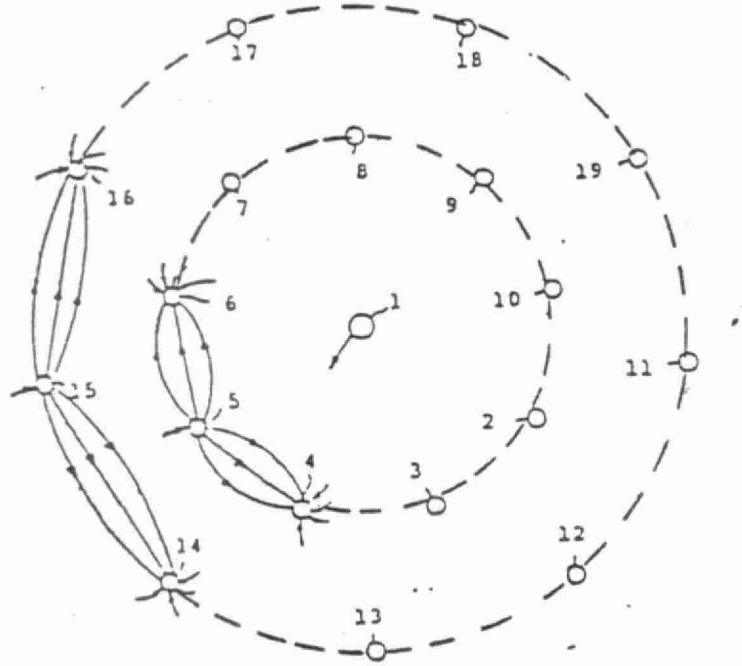

Fig. 8

1. Production well
2-10. Injection wells on the oxidation ring
11-19. Injection wells on the reduction ring

For reduction in connection with the microorganisms a suitable oxygen consuming substance is intermittent, for instance methanol in the reduction ring, and for the oxidation ring degassed aerated water is intermittently injected.

Due to the anisotropy and inhomogenity of the normal aquifer it is important to control the in situ processes in each sector around the production well. In observation wells situated outside the big reduction ring, between the two reduction and oxidation rings and between the small oxidation ring and supply well, redox electrods are installed.

Redox measurements are made from these redox electrods and the whole plants are fully automatic guided (fig. 9).

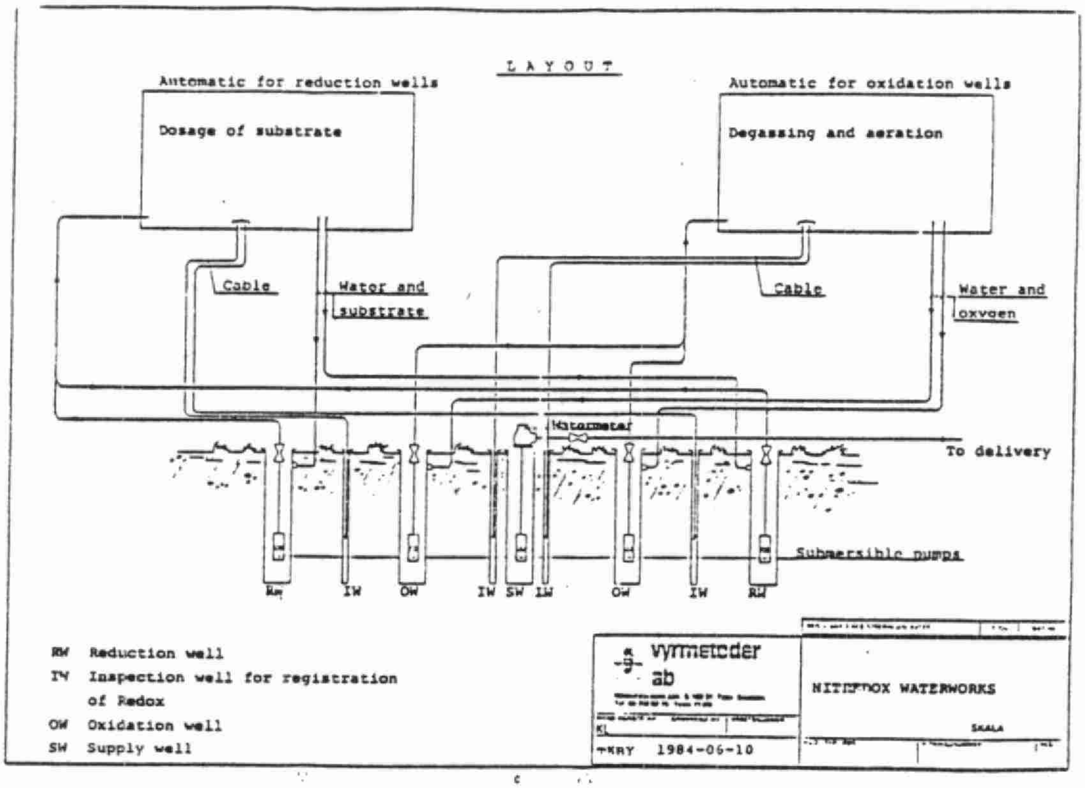

Fig. 9

The principle of the method itself works according to the following. On two rings with different radius around a production well, there are some injection wells drilled. In each injection well a small pump is installed. The injection wells situated on the outer ring are used for reduction in a specific running and the injection wells situated on the inner ring are used for degassing the nitrogen gas and to oxidize the eventual rest-content of nitrite as well as iron and manganese. The running pattern of each ring is according to VYREDOX II.

NITREDOX - INSTALLATION DESCRIPTION

In Bisamberg, Austria, there are three supply wells quite near each other. Of these wells No 1 has high nitrate contents. The same applies for a well in approximately 1 km distance. In this NITREDOX plant well No 1 is treated. The yield is about 60 l/s.

The supply well is surrounded by 16 reduction wells in an outer ring with a radius of 18 m. Inside this ring there is a second ring of 8 oxidation wells with a radius of 10 m. A number of inspection wells are placed inside the respective rings to constantly monitor the redox values of the passing water. Added to this we have placed a number of

inspection wells outside the NITREDOX system to have reference values on untreated water in the aquifer (zero reference).

To regulate the actual running of the pumps in the infiltration and pumping phases, two complete systems have been installed in adjacent buildings. The first system controls the dosage of reduction material. The second system controls the oxidation wells. The control equipment for the evaluation of inspection well data (computerized and fully automatic) is housed in the same part of the building as the oxidation system of the NITREDOX plant. All the data can then be called off from the installed computer through a telephone connection. This data is then used for evaluation studies and supervision without frequent trips to the plant. If necessary up to several thousands of data can be collected per day and it can be stored in the computer for several years.

Today there are several NITREDOX plants on line and due to the severe pollution problems, above all with nitrate and nitrite, it seems there is a big need for this method in the future.

CONCLUSIONS

The problems that have occurred in connection with VYREDOX and NITREDOX methods are of the following kinds:

A. Unsatisfactory dimensioning and construction of wells. (At the plant in Grimsås, Sweden, there are two supply wells. Six injection wells are drilled around each supply well. The aquifer is unconfined and consists of quaternary deposits. It contains a thin layer of very fine stuff, d_{60}=0,11 millimeters. This layer was not revealed by the soil sampling previous to the well drilling. Thus too wide slot openings were chosen for the well screens, and the fine stuff entered into some of the injection wells and blocked their screens. When this was discovered the faulty injection wells were restored, and this led to an improvement of the efficiency ratio from about 5 to almost 10. This example demonstrates the importance of correctly constructed injection wells.)

B. Shortage of injection water. (This happened at a plant near Stockholm because the water consumption was raised. The automatic control system was programmed for one injection every week, but due to the increased consumption, the injections were prohibited throughout the year. It was not possible to extend the raw water capacity. The plant has to be used as a future reserve only.)

C. Mistakes in the running of the plant. (Sometimes a well is pumped a longer time between the injections than is instructed for VYREDOX I in the operational manual. This is acceptable only if it happens occasionally. If it occurs regularly, however, the precipitation finally may take place too close to the well during the prolonged pumping period. This in turn can lead to a reduction of the well yield caused by iron and manganese deposits on the well screen. The well then has to be cleaned, for instance by using a suitable weak acid.)

D. Imperfect location of the injection wells.

The problems that have arisen in connection with the applications of the method have been possible to eliminate without any extensive arrangements.

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SOUTH AFRICA

SOUTH AFRICA

EMERGING WATER SUPPLY TECHNOLOGY

AWWARF Code #: SA-01

PROJECT DESCRIPTION

Project Title:

THE DEWATERING OF SLUDGES USING A TUBULAR FILTER PRESS

Contact (name of person, organization, address, telephone):

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Project Description (Please attach a schematic diagram if appropriate):

INTRODUCTION

The treatment of raw water usually involves a coagulation and flocculation stage followed by clarification and filtration. The resultant sludge can contain up to 10% of the feed water to the plant. The solids concentration in the sludge stream is between 3 and 30 g/ℓ, depending on the chemicals used for clarification and the type of clarification equipment. Apart from the disposal problem associated with the relatively low concentration sludge stream, the flow contains a significant volume of potentially usuable water.

Studies on the use of the cross-flow microfilter process, using porous ceramic tubes (ref.1) and prous plastic tubes (ref.2), for the concentrating of inorganic slurries have been reported. A cross-flow microfilter, with woven fabric hoses as filter support, has been used for the concentrating of a range of water works sludges (ref.3).

In the slurry concentrating process, the slurry is pumped under pressure and at a high velocity (1.5 to 3 m/s) into the bore of the porous tube. The slurry solids are concentrated down the length of the tube as the slurry liquid filters through the tube wall. A high feed velocity is maintained in order to minimise the build-up of a cake layer on the inner tube surface and to maximise the liquid filtration rate.

In contrast, in the tubular filter press process, the rate of cake build-up is maximised by reducing the cross-flow velocity to about zero. The process is then designed and operated for maximum cake production.

In concept the tubular filter press process has two outstanding features (ref.4). Firstly, the cake is formed inside the self supporting tubes, hence filter plates, as required in other filter press processes, are not

required. Secondly, the tubular filter press produces a very much thinner cake (typically 3 mm) than other filter press processes so that filtration rates are correspondingly higher resulting in a reduction of the area required for filtration.

A prototype unit was constructed at the Umgeni Water Board's H D Hill Waterworks in order to investigate the full-scale operability and economics of the process. The unit was designed to treat the waste sludge resulting from the treatment of 30 Mℓ/d of surface water. The surface water treatment comprised coagulation with a polyelectrolyte (with the occasional addition of bentonite) and resulted in a sludge with a concentration and flow rate of approximately 23 g/ℓ and 50 kℓ/d respectively.

The unit was constructed between June and October 1986, and commissioning trials took place between November 1986 and January 1987.

TUBULAR FILTER PRESS DESCRIPTION

The process schematic diagram is given in Fig.1. The tubular filter press consists of a feed tank, a pressure pump, the filter tube array, a filtrate collection tray and sump, a tube flushing and cleaning pump and an automatic cake removal and tube cleaning system (the cleaning head and carriage).

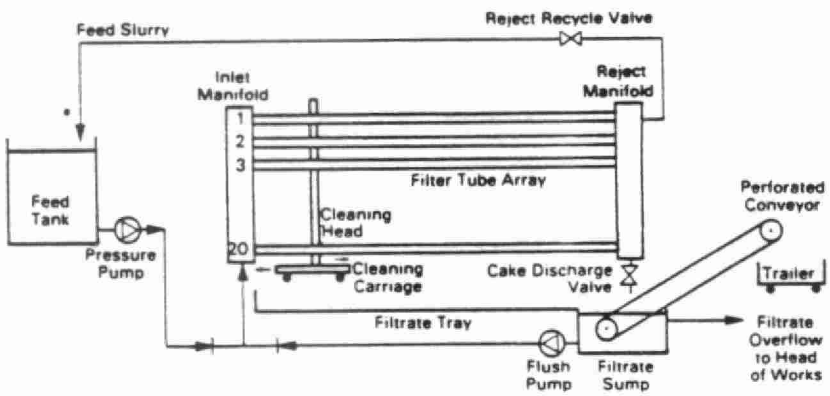

FIGURE 1: Tubular filter press process schematic

The tube array is made up of filter tubes woven from polyester yarn in a curtain and connected between an inlet and a reject manifold. The diameter of the tubes can range from 25 to 50 mm and the length from 10 to 20 m, depending on the application.

The feed slurry is pumped under pressure into the tube array against a closed reject recycle valve. As the pressure in the tube array increases the filtrate permeates through the tube walls and the slurry solids are deposited as a cake on the inner walls of the tube (Fig.2). The cake thickness increases with time and is monitored by measuring the filtration rate.

When the desired cake thickness has been achieved the outlet valve is opened and the flush pump started. The cake is dislodged from the inner tube surface by the action of the cleaning head moving along the tubes (Fig.3).

The cleaning head houses a pair of rollers which, when engaged, create a restriction in the tubes. The resultant high velocity and turbulence at the constriction dislodges the cake from the tube surface. The cake is then conveyed out of the tubes in the bulk fluid flow and is collected on a perforated conveyor belt.

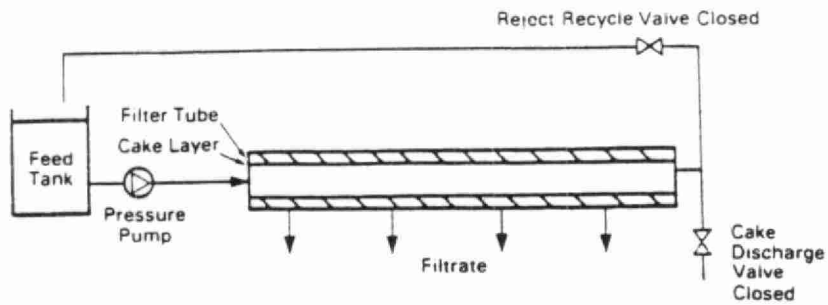

FIGURE 2: Single tubular filter press tube showing deposition of cake layer

A high-pressure water spray system has also been installed on the cleaning head in order to clean the filter fabric whenever necessary.

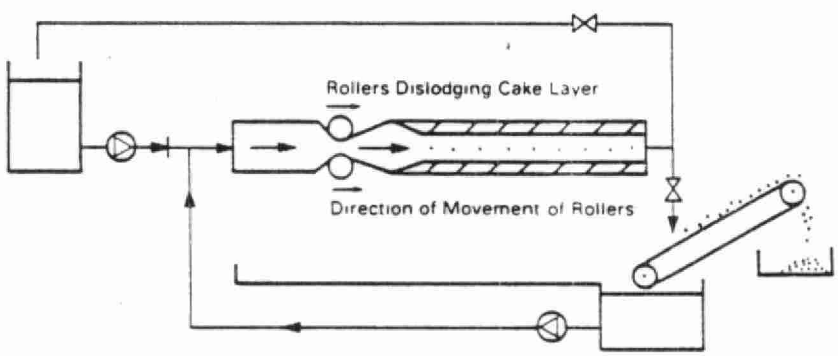

FIGURE 3: Rollers creating a restriction in the tubular filter press tube and dislodging the cake

The process operation is cyclic, each cycle consisting of a cake formation stage (typically lasting 10 to 60 min depending on the feed sludge concentration), and a cake removal stage (typically 2 to 4 min). Feed slurry is pumped under level control into the feed tank, filtrate is returned under gravity to the inlet of the water works and the cake is deposited in a trailer prior to dumping. The entire process is micro-processor controlled and requries a minimum of operator attention.

PROTOTYPE UNIT RESULTS AND TREATMENT CAPACITIES

Solids concentrations of the feed, filtrate and cake streams are given in Table 1.

TABLE 1 : Prototype unit : Feed, filtrate and cake solids analysis (bentonite/polyelectrolyte sludge)

	Feed susp.solids g/ℓ	Filtrate susp.solids mg/ℓ	Cake solids conc. % mass/mass
Mean	25	55	31
Range	2 tot 50	0 to 200	28 to 35

The cake production capacity of the prototype unit at various feed solids concentrations is given in Table 2

TABLE 2 : The effect of feed solids concentration on prototype unit cake production capacity at feed pressure of 400 kPa (bentonite/polyelectrolyte sludge)

Feed conc. g/ℓ	Process time min	Clean time min	Total cycle min	Cake per cycle kg dry/m^2	Prod rate kg dry/m^2.d
25	26	4	30	0,8	38
50	13	4	17	0,8	68
75	9	4	13	0,8	89

The estimated treatment capacity for various sized filter tube arrays is given in Table 3

The treatment capacity is directly related to the specific cake resistance of the slurry

TABLE 3 : Estimated cake production capacity for various filter tube array sizes at feed pressure of 400 kPa (bentonite/polyelectrolyte sludge)

Tube array dimensions				Cake prod. capacity per tube array tons/d dry solids	
Number of tubes	Tube diameter mm	Tube length m	Filtration area m^2	Feed solids g/ℓ	
				25	75
20	25	10	15,7	0,6	1,4
40	40	15	75,4	2,9	6,7
40	50	20	125,7	4,8	11,2

PROCESS CHARACTERISTICS

Low capital cost

The filter cake is formed inside the fabric tubes, thus avoiding the need for filter plates as used in standard filter presses. The cake thickness is approximately one fifth of that produced in conventional filter presses which reduces the filtration area. The tubular filter can be housed in a light industrial building.

Low operating cost

Power requirement is approximately 7 kWh/ton dry solids at a feed concentration of 25 g/ℓ and a pressure of 400 kPa. The process operates without chemical addition, is fully automated and self-cleaning and requires a minimum of operator supervision.

Cake and filtrate quality

The cake solids concentration is about 35% and is discharged in the form of finely divided flakes which are well suited to rapid secondary drying. The filtrate is suitable for recycling to the head of water treatment plant.

PROCESS DEVELOPMENT

The process was developed by the Pollution Research Group of the Department of Chemical Engineering, University of Natal under a Water Research Commission (WRC) funded project. A South African patent has been granted to the WRC (Patent No 87/0553) and applications have been filed internationally. The sole and exclusive worldwide licence has been granted to H.T.W. Hi-Tech Water N.V., whose sole sub-licencee for the Republic of South Africa is Explochem Water Treatment (Pty) Ltd.

The prototype was constructed under a joint agreement between the Umgeni Water Board, the Water Research Commission and the University of Natal. The project capital was provided by the Umgeni Water Board and the process design, construction and project management was undertaken jointly by the Umgeni Water Board and the University of Natal.

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EMERGING WATER SUPPLY TECHNOLOGY

AWWARF Code #: SA-02

PROJECT DESCRIPTION

Project Title:

DEVELOPMENT OF A PORTABLE TOXICITY DETECTOR FOR WATER

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Project Description (Please attach a schematic diagram if appropriate):

Several biological tests have been developed for determining toxicity in aquatic environments using fish, protozoa, algae and other freshwater and marine organisms. However, most of these test are relatively long and expensive and often require the time-consuming propagation of test organisms. As a result there is a general need to develop rapid, inexpensive and at the same time, sensitive tests to determine and monitor the toxicity of an ever-increasing number of complex chemicals being discharged to aquatic environments.

One of the most important mechanisms of toxic action within living material is the poisoning of enzyme systems. The inhibition of enzyme activity by waterborne toxicants adversely affects natural metabolic processes in biological organisms, the detection of which forms the basic for a number of systems evolved to assess the degree of aquatic pollution.

One rapid screening technique that has recently received attention is the bacterial assay (Microtox), which measures the decrease in natural light emmission from the luminescent bacteria Photobacterium phosphoreum in response to a toxic effect upon the enzyme luciferase. However, the instrumentation utilized thus far to monitor light output of such biochemical reactions, depends on the use of photomultipliers and photo-electric cells and is both energy demanding and expensive. Therefore, a new concept involving modern solid state electronic technology to detect light emissions has been employed to solve this problem.

A prototype light emission detector unit was fabricated and interfaced to a data acquisition and control module in order to evaluate the concept under laboratory conditions. Bioassays were conducted by measuring the decrease in luminescence of the bacterium Photobacterium phosphoreum in response to various toxicants. The detector unit detects toxic effects suc-

cessfully and its level of sensitivity compares well with standard bio-assays presently being employed.

A pre-production model luminometer has now been fabricated for laboratory simmulation testing and patenting has been requested.

EMERGING WATER SUPPLY TECHNOLOGY AWWARF Code #: SA-03

PROJECT DESCRIPTION

Project Title:

USER FRIENDLY COMPUTER PROGRAM FOR WATER SOFTENING AND STABILISATION

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Project Description (Please attach a schematic diagram if appropriate):

The chemical quality of a water can have a major impact on the system storing and conveying the water and in the use of the water. Waters from underground sources in dolomitic areas, for example, when brought to the surface, in contact with air, may become oversaturated with respect to calcium carbonate ($CaCO_3$) and cause extensive precipitation in storage dams, canals and pipes. Some waters may attack (be aggressive to) cement-like materials and/or cause corrosion of ferrous and other metals. Other waters, in municipal use, may be "hard" due to unduly high concentrations of calcium (Ca) and magnesium (Mg) ions giving rise to high soap demand in washing, furring of hot water cisterns and deleterious effects on some industrial processes. All these waters will need to be treated to remove or minimise the various adverse effects. The difficulty with any such a water is to assess its characteristics and to devise an appropriate treatment to give a non-scaling, non-aggressive, non-corrosive water.

Characterization and dosing estimation for waters is based on equilibrium chemistry of the calcium-magnesium-carbonate (Ca-Mg-CO_3) system. This is a complex weak acid/base system existing in three phases, gaseous, aqueous and solid. Both characterization and conditioning may require satisfying equilibrium in one, two or three phases (aqueous, aqueous-solid or gaseous-aqueous-solid).

Characterization and dosing estimation employing the basic mass and equilibrium equations defining the Ca-Mg-CO_3 system are cumbersome in the extreme and quite impractical. However, research workers have developed ancilliary mass parameters (e.g. Alkalinity, Acidity) that have greatly eased the problems of measurement for characterization and of estimation of dosing chemicals for conditioning.

A major advance in problem solving has been in the development of graphically aided procedures, to determine the characteristics of the water and

the dosing requirements. Using the graphically aided procedures, solutions have become readily obtainable and practical for field use. The development of the graphically aided procedures and their application to a wide range of conditioning problems has been dealt with in detail by Loewenthal et al (1986).

Even though graphically aided procedures are relatively simple their application still demands a fairly comprehensive understanding of the Ca-Mg-CO_3 system. At existing water treatment plants the characteristics of the raw water are known quite closely within a range but tend to change seasonally. In these situations the problem is to obtain the optimal solution which changes seasonally also. Finding the optimal solution often demands repeated trials which have to be done on a regular basis. In consulting practice a rapid assessment of alternative treatment procedures may be required. In all these situations even the graphically aided procedures are relatively slow. To assist in this regard, an interactive "user friendly" computer program has been written that gives answers rapidly as regards the characteristics of a water, its chemical conditioning and dosing requirements. The program should be adequate to provide solutions to the majority of problems the water chemist or engineer is likely to encounter in practice.

PROGRAM STRUCTURE

The program is executable on IBM compatible personal computers. The program is structured to promote interaction with the user. It first requests the name of the water source and any additional pertinent information and also a file name for storing the input and information that the program generates in its calculations for the requested treatment of the water. It then displays a "menu" of tasks (softening, stabilization, blending, etc) from which the user selects the task to be performed. On selection of the task the program prompts the user for the required measured input parameters relevant to the task e.g. total alkalinity (i.e. H_2CO_3 alkalinity or Alkalinity, Alk), Ca and Mg, pH, Total Dissolved Soldids concentrations (TDS) in mg/ℓ or conductivity, and termperature. From this information it calculates, and displays, associated parameters that assist in characterizing the water, i.e. ionic strength, total acidity (i.e Acidity), Langelier Index (LI) and Precipitation Potential (PP). Having characterized the water, depending on the task, options on the chemicals that may be added for conditioning are presented for selection. The program then calculates the mass concentration of dosing chemicals and the final state of the conditioned water, and displays the results. Depending on the task there are variations in the input, the derived information and the display, the reasons for which will become readily apparent to the user.

REFERENCE

R.E. Loewenthal, H.N.S. Wiechers and G vR Marais, Softening and stabilisation of municipal waters. Prepared for the Water Research Commission, 1986.

EMERGING WATER SUPPLY TECHNOLOGY AWWARF Code #: SA-04

PROJECT DESCRIPTION

Project Title:

THE APPLICATION OF TUBULAR REVERSE OSMOSIS WITH LIMITED PRETREATMENT FOR RECLAIMING SECONDARY PURIFIED SEWAGE

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Project Description (Please attach a schematic diagram if appropriate):

The City of Port Elizabeth treats 90% of its sewage in the Fishwater Flats Works which was designed with water reclamation in mind. The sewerage network collects separately from predominantly domestic and predominantly industrial areas and this separation is maintained throughout the liquid purification process. Tertiary treatment, therefore, can be applied to an effluent which is largely domestic in origin. At the present time tertiary treatment, consisting of rapid sand filtration and chlorination, is applied to about 5Mℓ/day of secondary effluent to produce a second-class industrial water used by two industries and on the sewage works itself. The demand for this grade of water, however, has proved disappointing, in spite of a low tariff. Industrialists find that the dissolved solids content of the water is too high for many purposes and the need for a separate retriculation system (because the water is not potable) is another negative factor.

It has become clear that a large-scale and economic outlet for reclaimed water from Fishwater Flats will only be found if treatment to potable standard is viable. Any reclamation process has to include demineralization because the secondary effluent at Fishwater Flats contains 600-1000 mg/ℓ of dissolved solids, with an average of 750 mg/ℓ. For this reason, a pilot scale (30 m^3/day) tubular, cellulose acetate, RO unit was commissioned in 1983 to investigate the possibility of reclaiming potable quality water from the tertiary treated water referred to above. Once RO was chosen for the demineralization step, the question arose whether it could also remove organic pollution without extensive pre-treatment. If so, the currently available physico-chemical reclamation processes, which are operationally complex, could be much simplified. Also, once reverse osmosis had been selected as the core of the process, the choice of the specific tubular RO system was not difficult because its unique cleaning system, based on flow reversal, seemed to offer the best opportunity for the control of fouling.

The pilot plant reached a running time of 15 000 hours. The results have been encouraging and indicate that, with sufficient attention to membrane cleaning, the system has the potential to produce potable water from secondary sewage effluent, consistently and economically, with only rapid sand filtration and chlorination as pre-treatment.

Despite the successful results obtained with the pilot plant, there are a number of factors requiring investigation before this method of water reclamation can be applied in practice. These factors concern the problems which arise in full-scale operations and which cannot be adequately assessed in pilot-scale experiments. For this reason a joint development project between the Water Research Commission and the Port Elizabeth Municipality has been launched, using a 500 m^3/day RO unit which will be operated for a period of three years to investigate :

(i) Full-scale operational procedures.

(ii) The quality of the product water, including micro-pollutants, toxicity, mutagenicity and pathogens.

(iii) The maintenance of potable water quality under full-scale operating conditions, including the development of "fail-safe" surveillance.

(iv) Operating costs at full-scale.

These investigations will initially be carried out on filtered, chlorinated secondary sewage effluent but, subject to satisfactory results with the pilot plant, will be continued on an unfiltered, unchlorinated feed. The plant has so far operated for 1 200 hours.

SPAIN

SPAIN

PROJECT DESCRIPTION

DEVELOPMENT OF ADAPTED BIOLOGICAL WASTE WATER TREATMENT PROCESSES UNDER MEDITERRANEAN ENVIRONMENTAL CONDITIONS

A research project is being carried out at the Universidad Politécnica de Madrid to further scientific knowledge in the field of biological waste water treatment and establish specific design parameters for use by engineers in the construction of waste water treatment plants in southern Europe. The project aims at developing biological waste water treatment processes tailored to the Mediterranean or similar climates. Both conventional and advanced waste water treatment processes are studied, with special emphasis on biological nitrification, denitrification and phosporous removal.
This first phase involves research on single and double stage processes, to attain optimum results with respect to nitrification and organic compound degradation.
Denitrification and phosporous removal are dealt with in the second phase in 1988.
This paper sets out the various possibilities for biological waste water treatment, together with the aims and development of the project and the results attained so far.

Centro de Investigación Madrid, with the participation of the Institut fur Siedlungswasserwirtschaft der RWTH Aachen and the Laboratorio de Ingeniería Sanitaria y Ambiental, E.T.S. de Ingenieros de Caminos, Canales y Puertos. Universidad Politecnica de Madrid.

Water, given its scarcity, must be considered as an economic commodity. In view of the increasing pollution level in the resources it contains, the research being undertaken by the O.T.U.M.A. Department of the Universidad Politecnica de Madrid is channelled towards pollutant reduction and nutrient removal.

The differing environmental conditions, e.g. climate, in southern and central Europe exercise a considerable influence on biological waste water treatment, and it is therefore necessary to study the efficiency of the various biological waste water treatment processes under these different conditions, revising and adapting the dimensioning bases and the design parameters.

Environmental reasons, progressive pollution and future increases in the demands regarding waste water treatment, in various countries including Spain, make it necessary to study not only conventional but also highly efficient advanced waste water

treatment processes, with a view to nutrient removal (N, P).

SCIENTIFIC AND TECHNICAL SITUATION IN THE FIELD OF URBAN WASTE WATER TREATMENT

Conventional waste water treatment processes

At present the majority of conventional waste water plants consist of a mechanical pre-treatment system (screening, grit and degreasing chambers), a primary treatment (primary separation) for the separation of solids and a biological stage consisting of an active sludge or trickling filter biological reactor, followed by a second separation. Both use the capacity of the micro-organisms present in the waste water, which degrade organic compounds in their metabolic processes, thereby forming cellular matter and sludge deposits.

These systems are used almost exclusively to deal with normal cases of urban waste water treatment. It is anticipated, however, that a number of alternatives will arise from the abovementioned biological processes.

The efficiency of a waste water treatment plant is measured by either the decrease or the concentration of BOD5 in the plant's output. The separators are calculated on the basis of the ascensional velocity and retention time, and the biological reactors on the BOD5 load. The BOD5 volume charge (VC) is a fundamental parameter, indicating the kilograms of BOD5 treated per m3 of the volume of the biological reactor in one day. The sludge loading ratio (SLR), indicates the relation between the pollutant load to be treated and the active biomass.

The term "advanced waste water treatment" is used for all variants which, apart from BOD5 removal, are intended to remove persistent substances and eutrophicating compounds (phosphorous and nitrogen compounds).

To quantify the persistent organic substances (either non-degradable or difficult to degrade), the Chemical Oxygen Demand (COD) is used.

ADVANCED WASTE WATER TREATMENT PROCESSES

Advanced waste water treatment may be carried out using either conventional plants with very low-load biological reactors or multi-stage plants.

If waste water is to be discharged into an outflow channel where there is a danger of eutrophication, the phosphorous compounds, at

least, must be removed by means of chemical processes (precipitation). There are, however, also some biologicial processes which attain a high level of phosphorous removal (3,4).

The removal of nitrogen compounds (ammonium, nitrite, nitrate) is equally necessary, although for different reasons. The presence of ammonium in rivers consumes large amounts of oxygen which can lead to an oxygen shortage if the water temperatures are very high and the flow is light, thereby causing the death of fauna. At the same time, if the pH values increase slightly, part of the ammonium becomes ammonic, which is poisonous to fish . The presence of ammonium also makes the treatment of drinking water more difficult.

High contentrations of nitrate in drinking water are harmful, especially to children (2,5).

Ammonium may be partially - or completely - removed in low-load plants. In the biological nitrification process the ammonium is changed into nitrite by means of Nitrosomonas-type bacteria (6,7, 8):

$NH_4 + 1.5\ O_2 - NO_2 + 2\ H_2O + 2\ H$ + energy

and to nitrate by means of Nitrobacter-type bacteria:

$NO_2 + 0.5\ O_2 - NO_3$ + energy.

This process is dependent on the age of the sludge, the active sludge process and the water temperature.

The abovementioned transformations require the presence of dilute oxygen, as each mg of NH_4-N oxygenated to NO_3-N consumes 4.57 mg of oxygen. It is consequently necessary to cover this demand, as well as the oxygen consumed by the micro-organisms for the degradation of BOD5.

Under the climatic conditions in central Europe, strong nitrification is obtained with sludge loading ratios of less than 0.15 kg BOD5/kg MLSS - d.

In the nitrification process the ammonium is converted into nitrate, but the nitrogen is not removed from the water. This occurs in the course of the denitrification process, changing the nitrate into gaseous molecular nitrogen. Almost all the heterotrophic micro-organisms are able to carry out the denitrification process, i.e., the bacteria which also perform the degradation of organic components (9). The denitrification process entails the absence of dilute oxygen and a sufficiently high concentration of organic compounds. Denitrification takes place in an active sludge plant, creating anoxic zones or reactors.

High denitrification levels are not obtained in trickling filter plants because of the aeration requirements of the biological film.

It may be said, in general terms, that the nitrification process is more stable in double stage biological plants than in single stage low-load plants. Denitrification is impossible in the second stage of double stage plants if the BOD5 yield is high, because in this case the remaining concentration of organic compounds is not low enough to carry out the process. Denitrification of the nitrate formed in the second stage of double stage plants requires a BOD5 yield of less than 60% (10). This may only take place in very high-load stages.

In Spanish population centres of more than 10,000 inhabitants, there is currently a tendency towards the construction of plants with a sludge loading ratio of 0.30 kg BOD5/kg MLSS - d (11,12). There are very few trickling filter plants.
Very low-load biological plants are already being installed in Germany and other central European countries. On the one hand, the lower load permits a very high yield; on the other, it requires greater reactor volume and higher energy consumption.

In Germany, double stage biological processes are also used in order to meet the high demands for water protection and make savings in investment and running costs.

The A-B process is a double stage process featuring a first stage of very high-load active sludge (stage A, SLR $\geq$ 2.0 kg BOD5/kg MLSS - d), and a second stage of low-load active sludge (stage B, SLR = 0.15 $\div$ 0.60 kg BOD5/kg MLSS - d). The recirculation systems of the two stages are strictly separate (13 ,14). This process is already being used in numerous large-scale treatment plants with very good results(15). As well as increased efficiency with greater process stability - including nitrification and denitrification - compared with conventional active sludge plants, the advantages of the A-B process include a reduction in investment and running costs, smaller reactor volume and the minimization of energy consumption(13,14,15).

The replacement of the B stage by a low-load trickling filter plant creates the A-T process, which also gives very good results (16).

RELATIONSHIP BETWEEN SLUDGE LOADING RATIO AND YIELD

In the case of waste water treatment plants operating under central European conditions, effluent quality and process stability bear a clear relationship with both the sludge loading ratio (SLR) in active sludge plants, and the volume charge (VC) in trickling filter plants.

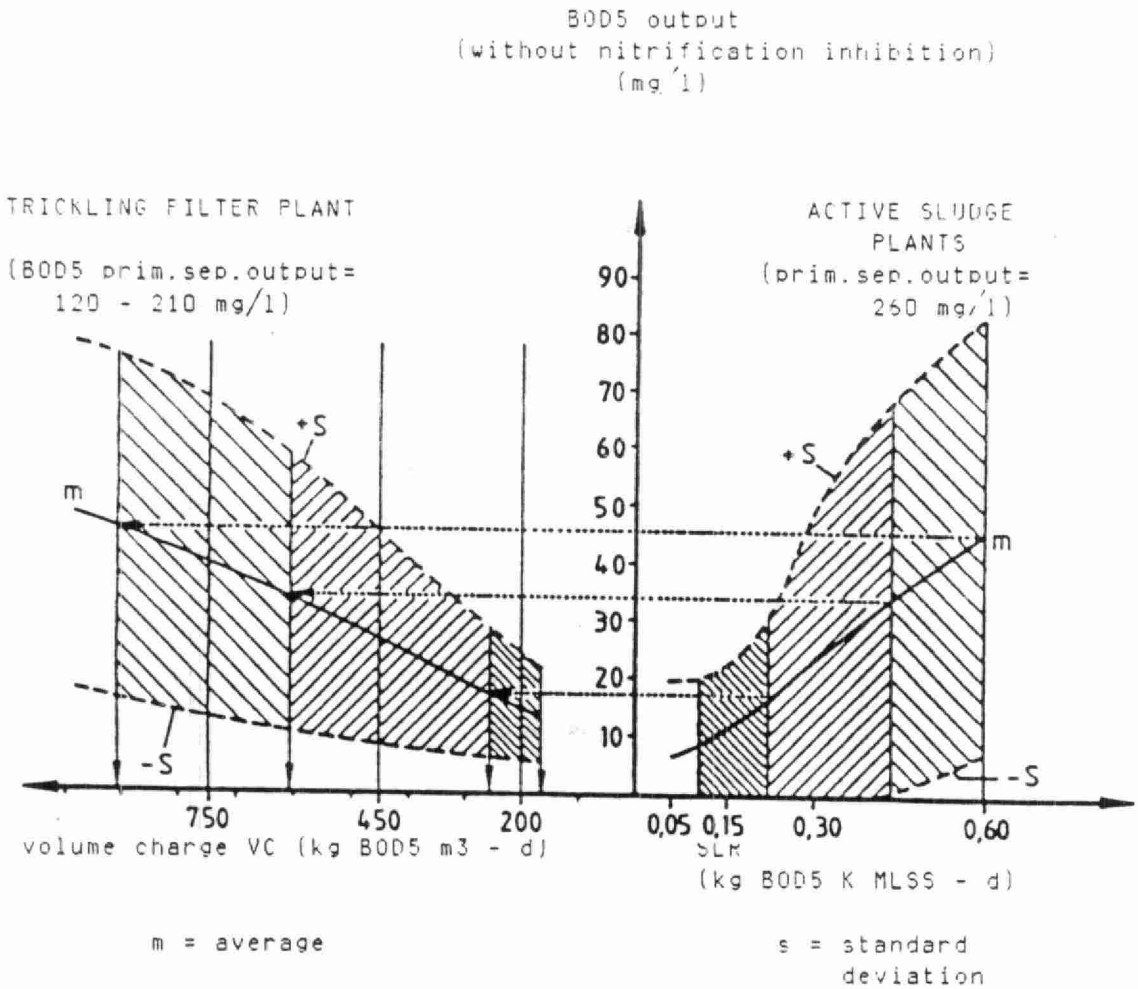


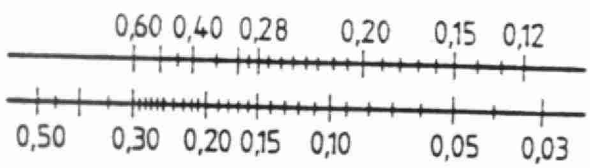
FIGURE 1

Statistic evaluation of output concentrations obtained in numerous studies carried out in 119 active sludge plants and 28 trickling filter plants in central Europe (17).

Figure 1 shows this relationship in the case of active sludge processes. This evaluation is based on a variety of data from several plants. The variation in output concentrations according to the characteristics of the waste water should be taken into

account.

Stage B of the A-B process



Single stage
Active sludge plants

Comparability of sludge loading ratios SLR (kg BOD5 kg MLSS - d)

FIGURE 2

Modification of the necessary sludge loading ratio of a B stage compared with a single stage plant to obtain the same BOD and COD yield (18).

Figure 2 compares the sludge loading ratios of the second stages (stage B) of the A-B process, with the corresponding SLRs for single stage plants. The output concentrations of the two processes must be the same to make this comparison. This means, for example, that the same yields are obtained from an A-B process with a sludge loading ratio of 0.60 kg BOD5/kg MLSS - d and a conventional plant with a sludge loading ratio of 0.30 kg BOD5/kg MLSS - d (18).

The relationships set out above are valid, but they may not be applied indiscriminately to Mediterranean climatic conditions with waste water temperatures of up to 30°C. It is known that the activities of the micro-organisms depend to a large extent on the temperature. For example, the nitrification velocity increases by 63% in a temperature of 20•C, as compared with the velocity at 15° C (10).

Furthermore, under other climatic conditions, fundamentally different biocenosis with other characteristics may be formed, with correspondingly different degradation speeds and form of sedimentation. The effectiveness of the waste water treatment in the different load sectors (low, medium, high) may therefore be considerably influenced.

OBJECTIVES OF THE STUDY

Based on the need to protect Spanish resources with regard to drainage and international waters, tests are being carried out at a pilot plant made up of modular elements to try to develop waste water treatment processes which are suitable for the Mediterranean or similar climates. This study is based on proven waste water treatment processes used in central Europe, involving single and double stage systems, and aims to define efficiency under Mediterranean conditions, with special emphasis on nitrification.

The most important differences in tests undertaken in central Europe are as follows:

- considerably higher average temperatures;

- greater variations in the winter/summer and day/night temperatures;

- different waste water composition, and

- very wide variations in flows and loads in tourist centres.

These differences exert a considerable influence on the biological treatment processes, and this is why studies are being carried out on the different components of the biological treatment of waste water, such as organic carbon removal, nitrification, denitrification and phosphorous removal with load variation. The findings will be used to draw up theoretical parameters for the design of waste water treatment plants, considering the possibility of staggered construction, the extension of existing plants and the optimization of design with respect to load variations due to tourism etc.

The first part of the study, concluded in January 1988, dealt with single stage processes:

- active sludge;

- trickling filter.

A grit chamber and a primary separation were employed in each case (see Fig. 3).

Tests were also carried out with two stage systems (see Fig. 4):

- very high-load active sludge - low-load active sludge;
- very high-load active sludge - low-load trickling filter.

The water is taken from the grit chamber of the "La China" municipal treatment plant in Madrid. The process provides for a sludge recirculation system to the first stage reactor, with pre-treatment steps, and a high-load active sludge reactor system from the primary separaton. In this way, without increasing the work volume of the whole treatment plant, two stage biological waste water treatment processes are achieved (process A-B, process A-T).

One aim of the project was to acquire a basic knowledge with respect to the BOD5, COD and nitrification parameters, in relation to the volume charge, the sludge loading ratio and the retention times.

Special attention was given to the characteristics of the active sludge, with the aim of optimizing the sludge sedimentation possibilities, depending on the biocenosis relevant to the techniques of the process and on the relevant load.

The efficiency of the plant drops considerably in the case of the appearance of floating sludge in the second separation. This frequently occurring problem arises as a result of bad active sludge separation processes in Spanish single stage plants with a sludge loading ratio of around 0.30 kg BOD5/kg MLSS - d. Possibilities are therefore being studied to improve the characteristics of the sludge to avoid the problem of solid discharge.

The second part of the study, begun in February 1988, deals with nitrogen removal (nitrification and denitrification) and biological phosphorous removal, with slight modifications to the equipment and operation of the pilot plant. Furthermore, it is planned to complete the pilot plant in a way which also allows sludge treatment to be studied, with previous stages within the digestive process itself.

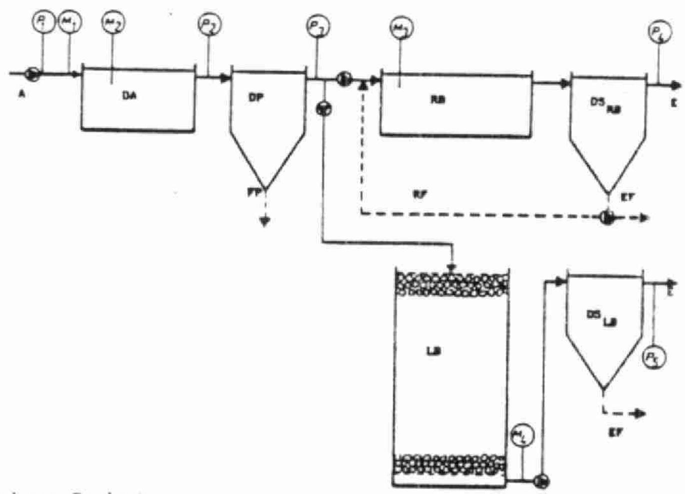
The findings obtained, together with the overall results of the study at the end of the project, will provide precise knowledge with respect to biological waste water and sludge treatment under these environmental conditions.

Exact design parameters will be set to enable the dimensioning of waste water treatment plants in relation to the desired quality of discharged water and the receptor channel. These parameters will offer an optimum solution as regards both operation and cost, thereby substantially improving the level of protection with respect to both water quality and hydraulic resources.

PROCESSES DIAGRAM

Active Sludge Plant (single stage)

Trickling Filter Plant (single stage)



P	Sampling Point	
M	Measurement Data	
A	In#low	
DA	Aerated Grit Chamber	PLANT:
DP	Primary Separation	Active Sludge
RB	Biological Reactor (active sludge)	(single stage)
DS RB	Secondary Separation	
DA		PLANT:
DP		Trickling Filter
LB	Trickling Filter	(single stage)
DS LB	Secondary Separation	
FP	Primary Sludge	
EF	Excess Sludge	
RF	Sludge Recirculation	
E	Outflow	

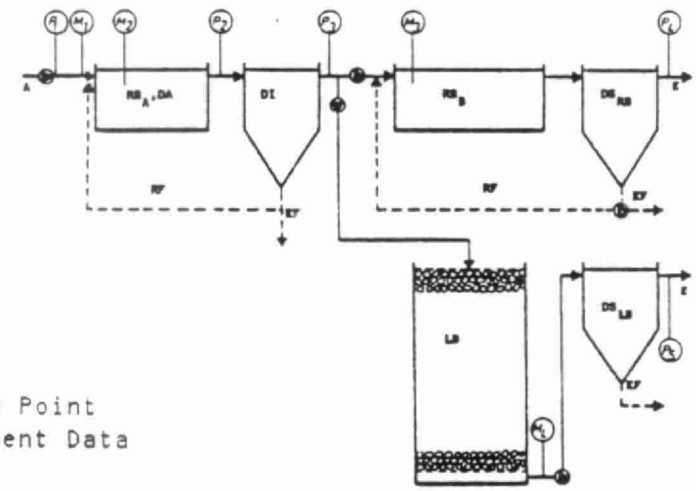
FIGURE 3

Diagram of pilot plant in single stage operation mode.

PROCESSES DIAGRAM

High-load Active Sludge - Low-load Active Sludge

High-load Active Sludge - Low-load Trickling Filter



P	Sampling Point		
M	Measurement Data		
A	Inflow		
RB_A, DA	Biological Reactor High-load Active Sludge and Aerated Grit Chamber	First Biological Stage	PLANT: High-load Active Sludge
DI	Intermediate Separation		-
RB_B	Biological Reactor Low-load Active Sludge	Second Biological Stage	Low-load Active Sludge
DS_{RB}	Secondary Separation		
RB_A, DA		First Biological Stage	PLANT: High-load Active Sludge
DI			-
LB	Trickling Filter	Second Biological Stage	Trickling Filter
DS_{LB}	Secondary Separation		
EF	Excess Sludge		
RF	Sludge Recirculation		
E	Outflow		

FIGURE 4
Diagram of pilot plant in two stage operation mode.

Table 1. Results of four phases of tests on single stage processes (average values, provisional evaluations)

Single Stage Process, Primary Separation (PS)

Phase	Input			PS Output			PS Yield		
	BOD5	COD	NH4-N	BOD5	COD	NH4-N	BOD5	COD	NH4-N
	mg/l						%		
I.1	314	557	-	165	323	26	47	42	-
I.2	276	574	25	173	405	24	37	29	4
I.3	210	530	-	152	329	32	28	38	-
I.4	213	489	30	161	316	26	24	35	13

Single Stage Process, Active Sludge Reactor (BR)

Phase	SLR	BR Output			Yield: BR Stage			Yield: PS+BR Total		
	Kg BOD5 / Kg MLSS - d	BOD5	COD	NH4-N	BOD5	COD	NH4-N	BOD5	COD	NH4-N
		mg/l			%					
I.1	0.40	52	109	4.4	69	66	83	83	80	-
I.2	0.24	62	148	4.0	64	63	83	78	74	84
I.3	0.28	25	154	3.8	84	53	88	88	71	-
I.4	0.21	19	81	3.5	88	74	87	91	83	88

Single Stage Process, Trickling Filter (BR)

Phase	SLR	BR Output			Yield: Trickling Filter			Yield: PS+TF Total		
	Kg BOD5 / m3 - d	BOD5	COD	NH4-N	BOD5	COD	NH4-N	BOD5	COD	NH4-N
		mg/l			%					
I.1	0.14	-	188	-	Pre-operating Phase					
I.2	0.13	49	132	11	72	67	54	82	77	56
I.3	0.12	33	127	16	78	62	51	84	76	-
I.4	0.10	39	115	12	76	64	54	82	76	60

DESCRIPTION OF THE PILOT PLANT AND TESTS

The pilot plant comprises the following parts:

	Volume
- 1 separator	400 ÷ 800 l
- 2 separators	1,200 ÷ 1,600 l
- 1 active sludge reactor/grit chamber	400 ÷ 600 l
- 1 active sludge reactor	1,000 l
- 1 trickling filter	13,000 l
- 3 compensator containers	120 l

as well as 7 waste water pumps, a blower, pipes, 4 samplers, OD, pH and temperature gauges and a computer system for data recording.

This equipment may be used to carry out the process tests set out in Figures 3 and 4.

Figures 5 and 6 show visual aspects of the plant.

In accordance with the test programme, the first part of the study (up to January 1988) includes operating the active sludge reactor with a sludge loading ratio of between 0.15 and 0.30 kg BOD4/kg MLSS - d and the trickling filter with a volume charge of between 0.167 and 0.230 kg BOD5/m3 - d in the single stage systems phase.

In the case of double stage systems, the first stage (high-load active sludge) has a sludge loading ratio of between 5 and 7.5 kg BOD5/ MLSS - d.

Table 2. Results of the test phase for double stage processes (average values, provisional evaluations)

Double Stage Process, First Stage (FS)

Phase	SLR	Input			FS Output			FS Yield		
		BOD5	COD	NH4-N	BOD5	COD	NH4-N	BOD5	COD	NH4-N
					mg/l			%		
II.1	3.3	182	448	23	58	174	17	68	61	24

Double Stage Process, Active Sludge Second Stage (SSS)

Phase	SLR	SSS Output			Yield					
					SSS			FS + SSS Total		
		BOD5	COD	NH4-N	BOD5	COD	NH4-N	BOD5	COD	NH4N
		mg/l				%				
II.1	0.21	11.5	65	2.0	80	63	88	94	86	91

Two Stage Process, Trickling Filter Second Stage (TFSS)

Phase	SLR	TFSS Output			Yield					
					TFSS			FS + TFSS Total		
		BOD5	COD	NH4-N	BOD5	COD	NH4-N	BOD5	COD	NH4-N
		mg/l				%				
II.1	0.04	9.7	47	2.2	83	73	87	95	89	90

The second active sludge reactor has a planned sludge loading ratio of between 0.15 and 0.5 kg BOD5/kg MLSS - d, and the trickling filter, operating on a parallel basis, has a planned volume charge of between 0.120 and 0.250 kg BOD5/m3 - d.

The temperature, pH and dilute oxygen data are recorded using software developed at the Institut für Siedlungswasserwirtschaft (Department of Sanitary and Environmental Engineering) in Aachen, and is stored on discs. The 4-channel gauge, with temperature compensation, used to measure pH and its transmission to the computer, was developed at the Department of Electrical Engineering at the Senior Technical School of Civil Engineering in Madrid.

The waste water samples are taken as 24-hour mixtures and are then analysed, in line with the relevant parameters, in the Laboratory of Sanitary and Environmental Engineering of the Senior Technical School of Civil Engineering. The analyses of environmental solids and sludge sediment volumes are carried out "in situ" at the plant.

The results of the analyses are entered into the computer and are stored on discs.

EVALUATION AND RESULTS

All the data material, obtained from the readings of the various measurement points recorded on disc up to 24 times a day, and from the analyses made on an almost daily basis of the water and sludge at the sample points, will be collated and evaluated by means of an evaluation programme developed especially for this purpose. This project was initiated in September 1987 and the results of the first stage of the study will be available in May 1988.

At the moment, therefore, only provisional, partial evaluations are available; these include all the values obtained from various parameters, with no suitability control.

So far eleven test phases have been carried out, six in single stage operation mode and five in double stage.

The results with respect to the most important parameters are set out in Tables 1 and 2. The values given are average values over 10 samples of a minimum of 24 hours, taken after the plant was declared ready for operation.

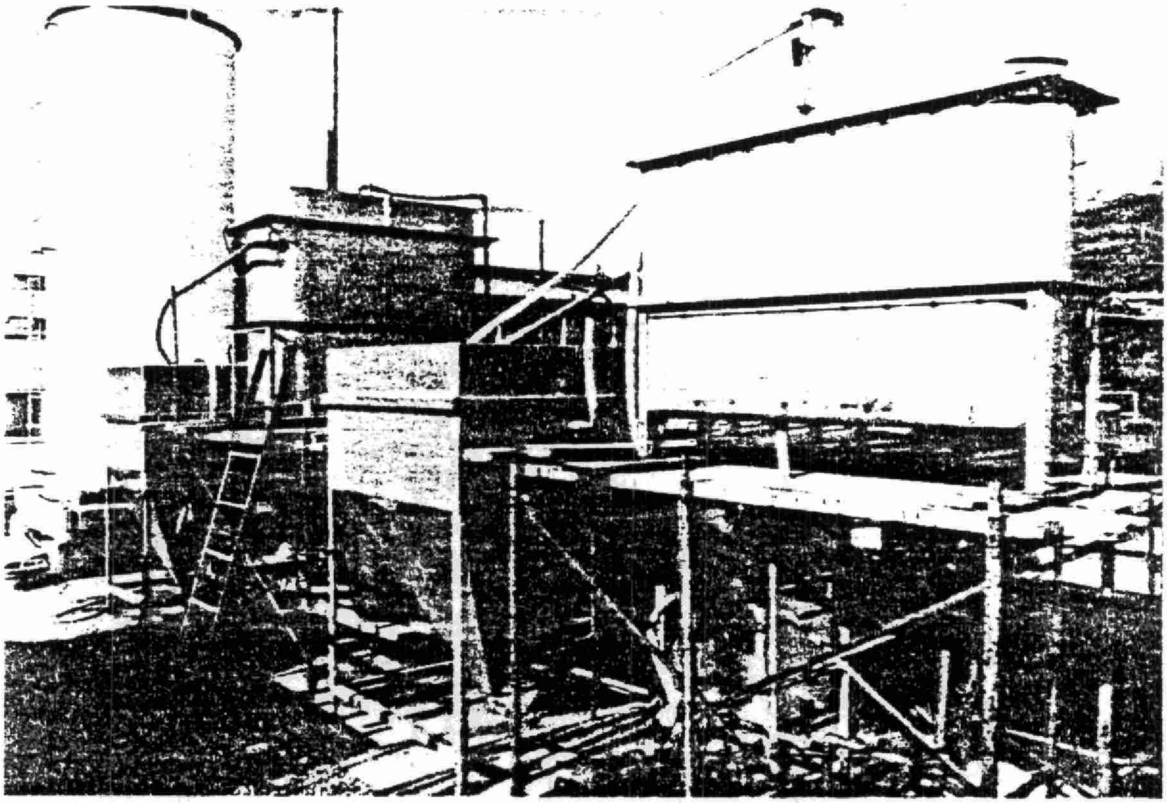


FIGURE 5

View of the pilot plant from right to left: grit chamber/high-load active sludge reactor, primary/intermediate separation, low-load active sludge reactor, secondary separation, active sludge reactor, trickling filter, mobile unit (with computer and guages).

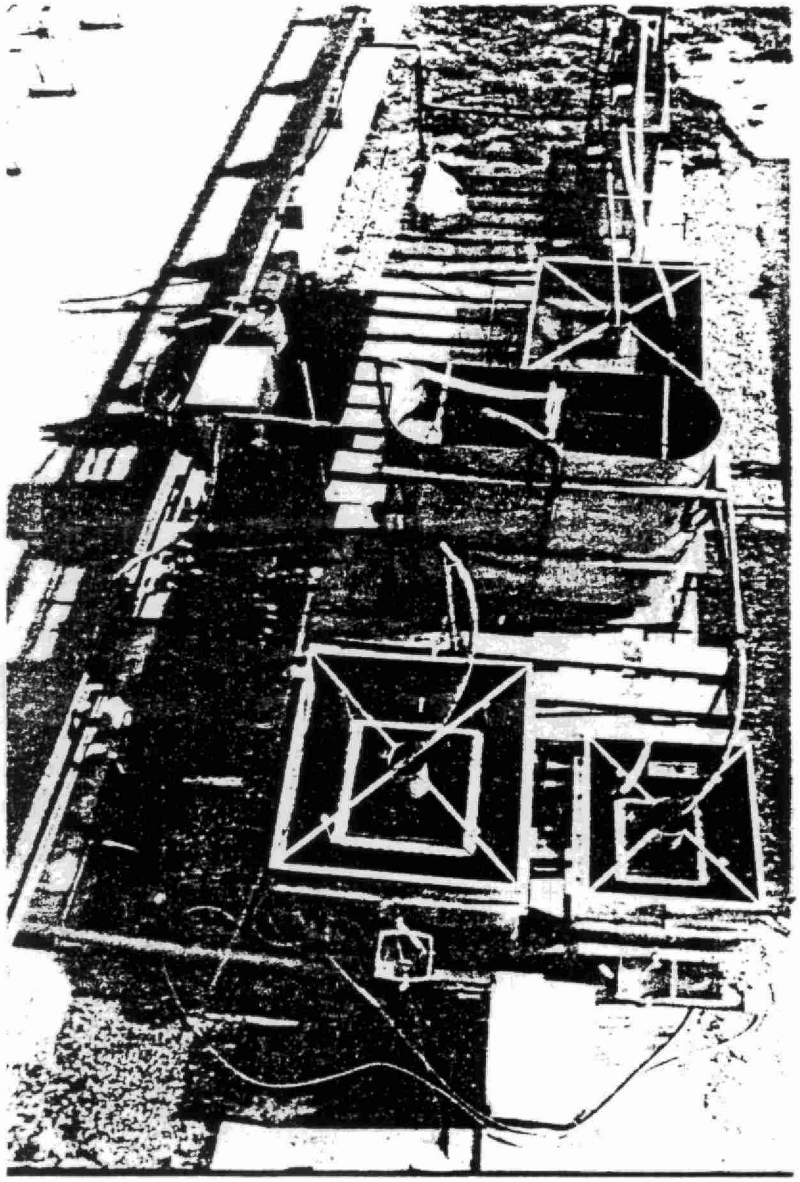


FIGURE 6

View of the pilot plant from the trickling filter from top to bottom: grit chamber/high-load active sludge reactor, primary/intermediate separation, low-load active sludge reactor, secondary separations of the trickling filter (left) and of the active sludge reactor (right).

It has been observed that the efficiency of the plant, as a conventional active sludge system with sludge loading ratios of between 0.2 and 0.61 kg BOD5/kg MLSS - d, is around 78-91% with respect to the BOD5 and between 71-83% with respect to the COD.

Operating the double stage active sludge system, with sludge loading ratios of between 3 and 8.6 kg BOD5/kg MLSS - d in the first stage, and between 0.2 and 0.8 kg BOD5/kg MLSS - d in the second stage, the efficiency is around 89-95% for the BOD5 and around 80-86% for the COD.

In the conventional plant with trickling filter and volume charges of between 0.1 and 0.3 kg BOD5/m3 - d, the efficiency is around 82-93% for BOD5 and between 76-87% for COD. The efficiency of the processes operating in series (active sludge in the first series with a loading ratio of between 3.0 and 8.6 kg BOD5/kg MLSS - d in the first stage and trickling filter in the second series with volume charges of between 0.04 and 0.2 kg BOD5/m3 - d), is around 94-96% for BOD5 and between 86-91% for COD.

Under summer conditions, with waste water temperatures of up to 26°, high levels of nitrification efficiency were attained in the double stage active sludge plant, even with high sludge loading ratios in the second stage. In winter, with waste water temperatures of 10-13°, the nitrification efficiency was 75% with a loading ratio of 0.35 kg BOD5/kg MLSS - d. These results are notably higher than the efficiency levels obtained in the conventional active sludge plant both in summer and winter.

The results given above are also borne out by the biocenosis. The volume of active sludge sedimentation in the single stage process (phase 1.4) was on average 915 ml/l (bulking) and 244 ml/l in the second stage of the double stage process, with the same loading ratio in both cases.

The volume of sludge sedimentation in stage A was 134 ml/l. With the MLSS at an average of 2.4 g/l, the Mohlman Index result was 54 ml/g for the first stage

The sedimentation behaviour of the sludge can be explained by the different characteristics of the biocenosis. The sludge in stage A contains only bacteria

The highly sedimentous sludge in the second stage (phase 11.1, SLR = 0.21) is very rich in species and as well as bacteria contains a wide variety of more developed organisms (see Figs. 10 and 11).

The sludge from the single stage plant (phase 1.4, SLR = 0.21) also contains bacteria and more developed organisms but in addition has large quantities of filamentous bacteria (see Fig. 12) which make it less sedimentous.

The good results obtained in phase 1.4 are largely based on the good fortune of always being able to maintain the sludge level in the second separation at between 1 and 5 centimetres below the separator output (see Fig. 13). It is interesting to note that the bulking disappeared shortly after changing from the single stage to the double stage process.

CONCLUSIONS AND PERSPECTIVES

The results obtained from the tests up until now in the first phase of the project show that the efficiency of the double stage biological processes, with a high-load active sludge reactor in the first stage and a low-load active sludge reactor (A-B process) or a trickling filter (A-T process) in the second stage, is greater than the efficiency of conventional single stage plants with respect to BOD5, COD, NH4-N and the sedimentation characteristics of the active sludge, while at the same time reducing the necessary volume of the work.

Very few modifications are necessary to extend the single stage processes, as it is sufficient to install an active sludge recirculation system between the aerated grit chamber and the primary separation, thereby creating a high-load active sludge stage formed by the active sludge reactor (which fulfils the function of the grit chamber at the same time) and the intermediate separator.

The provisional partial evaluations of the information available to date show that, in comparison with central Europe, nitrification occurs more quickly and with greater stability in the Mediterranean climate, especially in single stage plants.

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THIS STUDY WAS CARRIED OUT AS PART OF THE COOPERATION AGREEMENT BETWEEN THE INSTITUT FUR SIEDLUNGSWASSERWIRTSCHAFT DER RHEINISCH-WESTFALISCHE-TECHNISCHE HOCHSCHULE DE AACHEN (WEST GERMANY) AND THE UNIVERSIDAD POLITECNICA DE MADRID (E.T.S.I. Caminos, Canales y Puertos).

The development of low-cost biological waste water treatment systems suitable for the Mediterranean or similar climates, taking into consideration nitrification, denitrification and phosphorous removal, using modular elements, to optimize energy consumption in the waste water treatment process.

- THE STUDY WAS CARRIED OUT UNDER THE DIRECTION OF:

  Prof. Dr. Aurelio Hernandez Muñoz. Director of the Departmento de Ordenación del Territorio. Urbanismo y Medio Ambiente de la Universidad Politécnica de Madrid.

  Prof. Dr. Dr H.C., Botho Böhnke. Director of the Institut für Siedlungswasserwirtschaft der Rheinisch-Westfälischen Technischen Hochschule, Aachen.

- WITH THE PARTICIPATION OF:

  Engineers: M. Kröner, W. Kühn
  Laboratory: Aliro Estay (Chemist)
  Isabel del Castillo (Biologist)

  et alii.

SWITZERLAND

SWITZERLAND

PROJECT DESCRIPTION

Project Title:

Pretreatment of river water for groundwater recharge by horizontal roughing filtration and vertical sand filtration

Contact (name of person, organization, address, telephone):

Dr. M. Boller, M. Wegelin
EAWAG
Überlandstrasse 133
CH-8600 Dübendorf 01-823 50 47

Project Description (Please attach a schematic diagram if appropriate):

An existing river water treatment plant for artificial groundwater recharge should be upgraded in order to avoid excessive break-through of particulate matter into the underground and the subsequent danger of cogging of the recharge wells.
In a first step, the existing processes for solids removal have been carefully analyzed, besides other parameters also by particle analysis. With the help of model calculations, proposals could be made for enhancing the performance of the horizontal roughing filters. In a further study, two different solutions will be realized in full scale and their performance will be tested.

Operating and cost data (including data on efficiency, results, etc.):

Place(s) of installation/application (including dates):

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

PROJECT DESCRIPTION

Project Title:

Residual polyacrylic polymers in direct filtration.

Contact (name of person, organization, address, telephone):

Dr. M. Boiler,
EAWAG
Überlandstrasse 133
CH-8600 Dübendorf 01-823 50 47

Project Description (Please attach a schematic diagram if appropriate):

In a double filter system for direct filtration of a turbid spring water, the flocculation with poly-Al-chloride was enhanced by poly-acrylic polymers. The residual polymers after the first filter was measured by the so called Burchert-method and the further elimination in the second filter step after an additional of Al-dose, but no polymers, was controlled.
Another investigation concerned the residual polymer levels in a full-scale waste water filtration plant, where Fe Cl_3 and poly-acrylic polymers are combined in order to reduce phosphorus from the waste water.

Operating and cost data (including data on efficiency, results, etc.):

Place(s) of installation/application (including dates):

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

PROJECT DESCRIPTION

Project Title:

Smaller mobile and autonomous water treatment and packaging unit (400 C).

Contact (name of person, organization, address, telephone):

WATER-LINE Ltd
CH - 6849 Mezzovico-Lugano (Switzerland)

Tel. 091-953222 / Tlx. 844729 water ch / Fax. 091-952064

Mr. Ari Wöstenfeld, Marketing Manager

Project Description (Please attach a schematic diagram if appropriate):

+ photo and treatment process enclosed

The fully mobile and autonomous water purification unit is designed to treat surface and ground water and to package the obtained drinking water into sterile plastic bags of one liter for practical and hygienic storage and distribution.

The installation is provided with an autonomous generator but it's also equipped with an additional plug to be directly linked to the electrical network. Besides it includes a compressor, pumps, cables and flexible tubings, the fully automatic packaging system and accessories.

Production

400 bags per hour. The content may be chosen according to requirements (1 liter, 1/2 liter and 1/3 liter); The sterilised bags are very economical. The trated and packaged water may be safely stored for up to 5 years.

Though beeing small, this unit has a daily production capacity of 9000 bags (equal to 9 tons!).

WATER-LINE manufacturers larger units for same applications for a daily capacity of 25000 and 75000 bags.

Operating and cost data (including data on efficiency, results, etc.):

Manufacturing cost of one liter bag including amortisation of the unit is at present exchange rate US$ -.037 (Jan. '88).

*** Other cities suddenly struck by natural or ecological disaster realise too late that they should have opted for the WATER-LINE system already years ago.

Place(s) of installation/application (including dates):

All our units have produced excellent results in dozens of emergency situations like earthquakes (Frioul-Italy '76; Van Lake Region-Turkey '76; Montenegro-Yugoslavia '79; El-Asnam-Algeria '80; Naples-Italy '80; Mexico-City-Mexico '85), droughts (Florence-Italy '85) and chemical pollution of municipal water supply (Casale-Italy '86; Bergamo-Italy '86), ecc.

Many public administration and water authorities have acquired the WATER-LINE system to preventively produce and stock large quantities of bags in order to dispose of a ready supply in case of emergency.

SEE ***

Patent staus, if applicable:

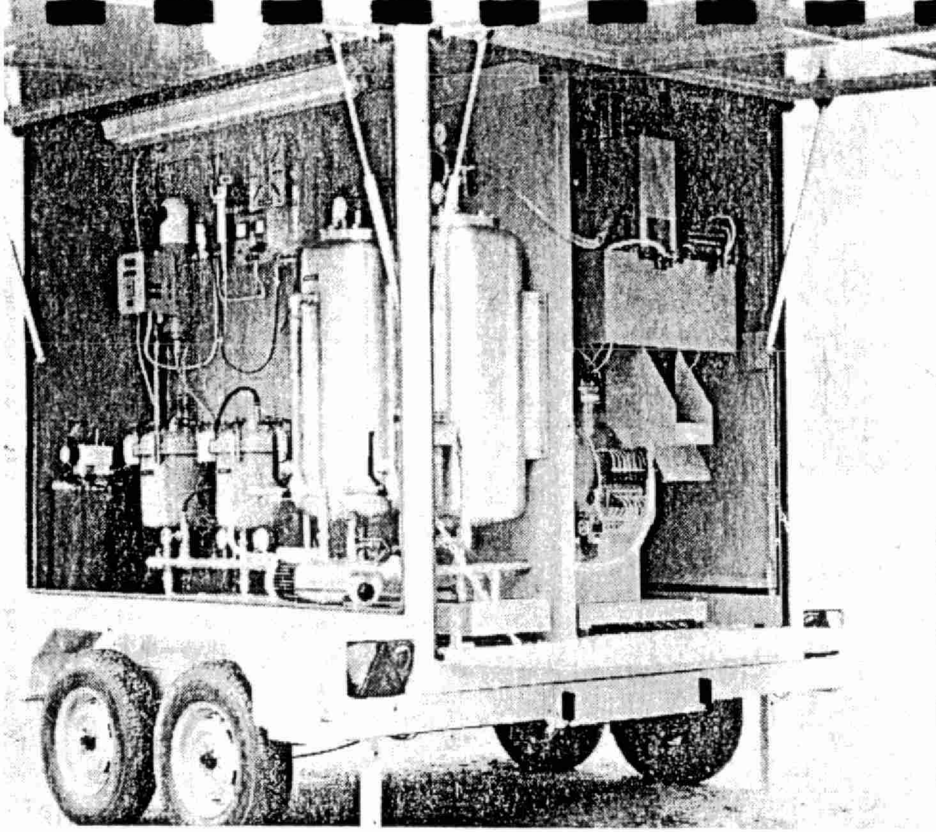
WATER-LINE owns a patent on mobile and autonomous treatment and packaging units.

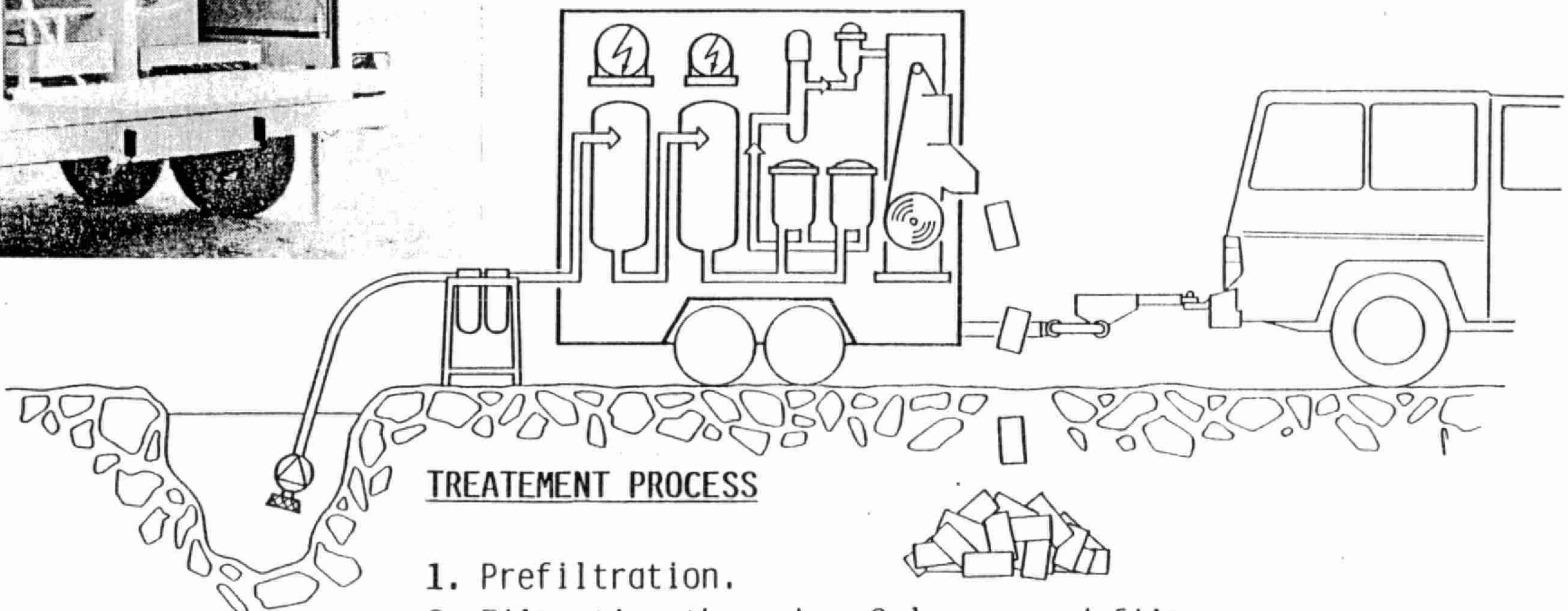
Other information (e.g., funding source, cooperating agencies, etc.):

WATER-LINE has developed their units with own technology and reasources.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

Minisupermatic "C"





TREATEMENT PROCESS

1. Prefiltration.
2. Filtration through a 2-layer sand filters of quartz and hydroanthracite.
3. Filtration through an activated carbon filter.
4. Microfiltration through ceramic candles.
5. Degermination by UV-Rays.
6. Conservation through silver ions.
7. Packaging of the water in 1 l, 1/2 l, 1/3 l PE bags.
8. On request: printing of the conservation date or issuing da

PROJECT DESCRIPTION

Project Title:

Low maintenance submersion dissolved oxygen sensor with self-cleaning electrodes.

Contact (name of person, organization, address, telephone):

Dr. A. Brugger

Züllig LTD

CH-9424 RHEINECK

Project Description (Please attach a schematic diagram if appropriate):

The operation of the dissolved oxygen probe is based on the chemical principle used by Toedt around 1940 for the determination of dissolved oxygen content in surface waters.

If a pair of electrodes consisting of two different rare metals, e.g. platin-cadmium, gold-zinc, etc. are submerged in an electrolyte solution, an electric current can be detected flowing between the electrodes whose magnitude is dependent, among other factors, on the content of dissolved oxygen in the solution. Such a pair of electrodes from a galvanic element in which a depolarization current flows which, according to Toedt, results from the following reaction:

$Me = Me^{++} + 2e^{-}$ $\quad$ $O_2 + 4e^{-} + 2H_2O = 4\ OH^{-}$

Me = e.g. Iron, Zinc

The most part of D.O. sensors are based on the galvanic cell system used by Toedt and utilize a membrane to separate the electrolyte and electrodes from the waste water. Membranes are subject to fouling and require a varying high level of maintenance.

The Züllig sensor has no membranes to replace and no filling solutions are required. This sensor design involves selection of electrode materials, electrode configuration and provision for continuous cleaning and flushing that eliminates the need for a membrane. The sensor is automatically temperature compensated in the range of 3-30° C to correct effects of temperature change on the electrical signal generated.

The sensor is comprised of a plastic tube fitted at its lower end with two concentric metal electrode rings (cathode, anode), insulated from each other, which are continuously grounded and polished by a rotating, spring loaded and isolated grindstone. This grindstone is continuously driven by an A.C. motor built in the probe. The electrodes are enclosed by a chamber which protects them from direct contact with oxygen bubbles and material suspended in the waste water. This chamber, so called "beaker", oscillates vertically and serves as a simple pump to continuously change the waste water sample that is in contact with the electrodes. The dissolved oxygen sensor is in full-scale use.

Operating and cost data (including data on efficiency, results, etc.):

The Electrode now consists of two individually inserted parts. So the contact pressure of the grindstone can be individually adjusted. Replacement of the grindstone will no longer be necessary before 5 - 12 months and the recalibration could be extended to 12 months.
For use in sewage treatment plants the back of the grindstone is automatically cleaned by a wiper to avoid the deposit of sludge. The new design for submersion use also permits a new approach in applying proven technic to oxygenation reactors and measurements at various depth (e.g. ground water wells or artifical lakes up to 100 feet below surface).

This new techniques provide a high measuring stability with very low maintenance.

Place(s) of installation/application (including dates):

Sewage and activated sludge:
- In oxygen reactors and sewage treatment aeration basins for the direct control or direct gas regulation in systems using technical oxygen.
- Monitoring of d.o. content in clarifiers and in sewage treatment works effluent.

Drinking water:
- Monitoring and control in ground water, reservoirs, water treatment plants and water filtration systems.

Surface water:
- Monitoring of dissolved oxygen especially in creeks, rivers, lakes and dams (up to 30 m depth).

Aquaculture: - Monitoring and control in fish-hatcheries.

Patent staus, if applicable:

CH - Patent No. 659.526
Europe - Patent No. 0.144.325
USA Patent No. 4.576.704

Other information (e.g., funding source, cooperating agencies, etc.):

Development: Prof. Dr. O. Jaag, Dr. A. Hörler, Dipl. Ing. L. Kalman
Federal Institute of Technology, Zürich, Switzerland

Further Development: Züllig AG, CH-9424 Rheineck

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

Low maintenance submersion dissolved oxygen sensors type SS 11 with self-cleaning electrode

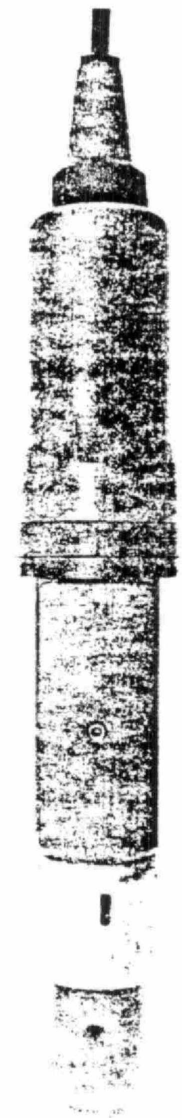


Figure 1
Züllig submersion d.o. probe type SS 11

Construction, characteristics and general applications

1. Development
The Züllig submersion dissolved oxygen sensors (new patent pending) represent a further development of the sensors type SS 3 "with the characteristic red motor housing". The SS 3 performs successfully since more than 10 years all over the world. The sensors are specifically designed to determine dissolved oxygen in watery solutions, especially such as in sewage treatment aeration basins, cleaned waste water, rivers and lakes. The new design for submersion use also permits a new simple approach in applying proven technic to oxygenation reactors and measurements at various depths. Furthermore applications exist in ground water wells and artificial lakes where the new sensors may be used up to 100 feet below surface.

Improved self-cleaning technique
The electrode, which is continuously cleaned by a grindstone, now consists of two individually inserted parts, the anode and cathode. Both of them have a plug-contact to the signal cable. The contact-pressure of the grindstone to the anode and cathode can be individually adjusted. With this, replacement of the grindstone will no longer be necessary before 5–12 months and the recalibration period could be extended to 12 months. The probe may be mounted in a guiding tube (Fig. 6) or with the new shaft-version (Fig. 7) which can be installed in the existing probe bracket (Fig. 8).

Outstanding features:
- Self-cleaning System
- Swiss patent No. 469981 and international patents (new patents pending)
- Low maintenance electrodes
- High stability and reliability over extended periods
- No membranes or filling solutions required
- Continual sample change minimizes electrode fouling
- Rugged construction
- Signal telemetering over distances of at least 600 feet without electronic amplification
- Submerged operation up to 100 feet

USA-Patent No. 4.576.704

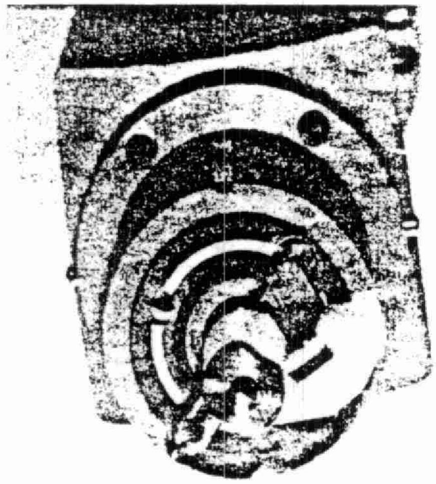


Figure 2
Bottom view of the electrode and grindstone (self-cleaning system)

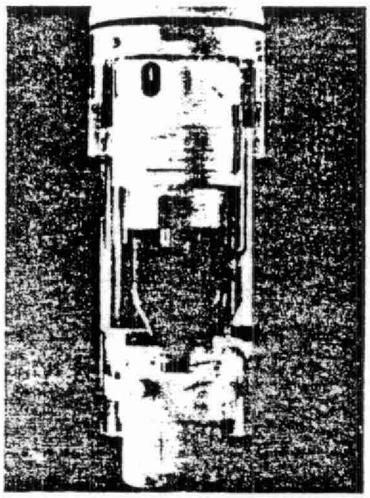


Figure 3
Pumping-beaker with expulsion system exposed

2. Applications

Sewage and activated sludge:
- In oxygen reactors and sewage treatment aeration basins for the direct control or direct gas regulation in systems using technical oxygen.
- Monitoring of d.o. content in clarifiers and in sewage treatment works effluent.

Drinking water:
- Monitoring and control in ground water, reservoirs, water treatment plants and water filtration systems.

Surface water:
- Monitoring of dissolved oxygen especially in creeks, rivers, lakes and dams (up to 30m depth).

Aquaculture:
- Monitoring and control in fish-hatcheries.

3. Operating principles

The operation of the dissolved oxygen probe is based on the chemical principle used by Toedt around 1940 for the determination of dissolved oxygen content in surface waters.
If a pair of electrodes consisting of two different rare metals, e.g. platinum-cadmium, gold-zinc, etc. are submerged in an electrolyte solution, an electric current can be detected flowing between the electrodes whose magnitude is dependent, among other factors, on the content of dissolved oxygen in the solution. Such a pair of electrodes from a galvanic element in which a depolarization current flows which, according to Toedt, results from the following reaction:

$Me = Me^{++} + 2e^-$ $\quad O_2 + 4e^- + 2H_2O = 4\,OH^-$

4. Construction of the submersible dissolved oxygen probe Fig. 3, 4

The most part of D.O. sensors are based on the galvanic cell system used by Toedt and utilize a membran to separate the electrolyte and electrodes from the waste water. Membranes are subject to fouling and require a varying high level of maintenance.
The Züllig sensor has no membranes to replace and no filling solutions are required. This sensor design involves selection of electrode materials, electrode configuration and provision for continuous cleaning and flushing that eliminates the need for a membrane. The sensor is automatically temperature compensated in the range of 3–30°C to correct effects of temperature change on the electrical signal generated.
The sensor is comprised of a plastic tube fitted at its lower end with two concentric metal electrode rings (cathode, anode), insulated from each other, which are continuously grounded and polished by a rotating, spring loaded and isolated grindstone. This grindstone is continuously driven by an A.C. motor built in the probe. The electrodes are enclosed by a chamber which protects them from direct contact with oxygen bubbles and material suspended in the waste water. This chamber, so called "beaker", oscillates vertically and serves as a simple pump to continuously change the waste water sample that is in contact with the electrodes.

Depending on the type of application two electrode combinations are being used and each electrode is single changeable: Fig. 5

Electrode combination
Silver-Amalgam (Cathode) and Iron (Anode) AE...
Silver-Amalgam (Cathode) and Zinc (Anode) AZ...

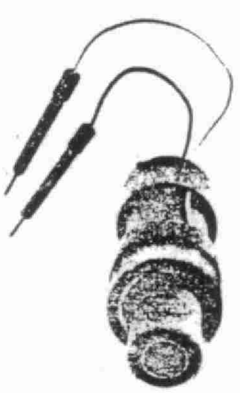
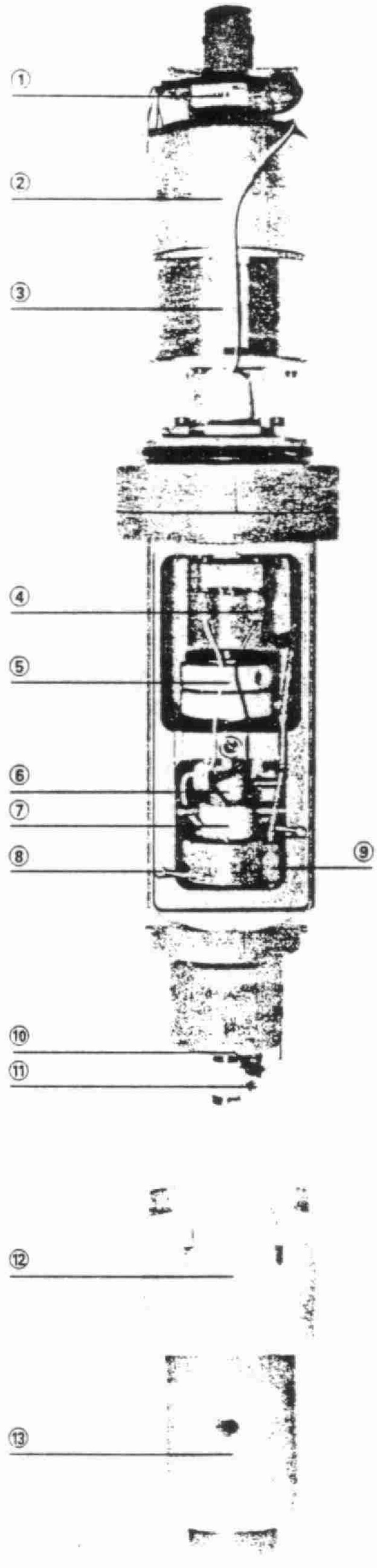


Figure 5
Single changeable electrodes



① connector assembly
② motor
③ gearbox
④ connectors for electrodes
⑤ coupling
⑥ anode holder
⑦ cathode holder
⑧ lock pin for adjustment of springs tension
⑨ thermistor
⑩ grindstone
⑪ backside cleaner
⑫ labyrinthring
⑬ beaker assembly

Figure 4

Grindstones
For application in sewage treatment plants, a non regenerating grindstone-combination type RH400, which is made of carborundum/rubber, is used. For application in drinking- and industry water as well as for surface measurements, furthermore in sewage treatment plants with small contents of grease and oil, a regenerating diamond grindstone type D-70 is used.

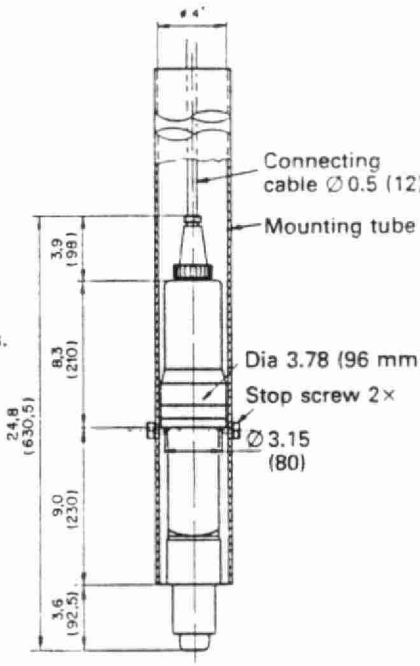


Figure 6
General dimensions in inches and mm ( )

5. Maintenance

Cleaning and replacing of electrodes and grindstones (Fig. 2)
To avoide the deposit of sludge, the back of the grindstone is automatically wiped by a cleaner. External cleaning and examination of the electrode/grindstone mechanism should be done when necessary. Do not remove the grindstone. The grindstone should normally be replaced every 5–12 months depending on the chemistry of the medium. Typical service life for the electrodes is 3–5 years.

Life expectancy	Probe-construction	15–20 years
	Electrodes	3– 5 years
	Grindstones	5–12 months
Check-up calibration	recommended after 12 months	
New calibration	always necessary after replacement of electrode	

6. Specifications

Dimensions:	
a) submersible type fig. 1/6	max. length 630 mm, max. diam. 96 mm
b) new shaft type fig. 7/8	max. length 1485 mm, max. diam. 96 mm
Shipping weight (without cable)	submersible type 3.4 kg shaft type 6.1 kg
Electrical power:	48 V, 6 VA, 50 cycles (power to the sensor motor from amplifier) Option: 48 V, 6 VA, 60 cycles
Standard cable length:	13 ft (4 m)
Weatherproof materials:	Plastic PVC, stainless steel (V4A) Delring and Epoxy Silver amalgam, iron or zinc
Temperature range:	
a) operational in water	3 to 30°C (temperature compensated)
b) storage temperature	−2 to 60°C
Measuring ranges:	
– Iron-electrode	0 to 15 ppm (mg/liter)
– Zinc-electrode	0 to 25 ppm (mg/liter)
Accuracy (better than):	±0.2 ppm (mg/l) at <0.5 m/s flow within D.O. range of 0–5 ppm ±0.3 ppm (mg/l) at <0.5 m/s flow for D.O. levels greater than 5 ppm

Dependence on cations and anions as well as other parameters

Possible interference parameters in solutions with starting value ≥ 600 µS/cm	Permissible maximum concentrations of interference parameters (ppm) for deviations of ≤ 0.2 ppm for electrodes type		Possible interference parameters in solutions with starting value ≥ 600 µS/cm	Permissible maximum concentrations of interference parameters (ppm) for deviations of ≤ 0.2 ppm for electrodes type	
	AZ...	AE...		AZ...	AE...
K^{+1}	>1000	>1000	Cu^{+2}	3.0	5.0
Na^{+1}	>1000	>1000	Ni^{+2}	0.1	>20
Mg^{+2}	>1000	>1000	Co^{+2}	1.0	3
Ca^{+2}	>1000	>1000	CN^{-1}	5.0	15
NH_4^{+1}	>1000	>1000	NO_3^{-1}	>1500	>1500
Al^{+3}	1.0	20	SO_4^{-2}	>1500	>1500
Pb^{+2}	2.0	3.0	S^{-2}	2.0	1.0
Cd^{+2}	5.0	5.0	PO_4^{-3}	>100	>100
Zn^{+2}	5.0	>30	Cl^{-1}	>2000	>2000
Cr_{tot}	>30	15	Anion-active tensides	~50	~50
Fe^{+2}	0.2	10	Crude oils	~2000	~500
Fe^{+3}	1.0	>20	Cl_2	0.5	1.0
Mn^{+2}	15.0	>30	pH	6.5–9	6.2–9

7. Protection against choking of the beaker caused by bulky solid matter:
e.g. for plants without pre-clarification.
For such applications, the standard-labyrinthring (no. 12, fig. 4) is replaced by a protection-screen (fig. 9).

8. Stability
(Sensitivity to various interferences)

a) Mechanical contamination
Due to the continuous cleaning action of the grindstone, which assures constant electrode surface geometry and continous uniform exposure of the metals to the medium, mechanical contamination of the electrode surface is inhibited and longterm constant measurement is guaranteed.

b) Flow velocity
Sensitivity of the electrodes to varying flow velocities of the medium is largely eliminated by the beaker surrounding the electrodes and the additional labyrinth-ring. Directed currents in excess of 0.5 m/s may affect the d.o. measurement, hence the probe needs a cylinder type K_2. The labyrinthring may be left off if measurement takes place in streams with low velocity.

c) Electrical induction
Because of the current measurement principle there is generally no major danger of inductive influence due to electrical power cables laid in parallel to the measuring cable provided that a twisted cable is used.

d) Chemistry
(Based on research and tests on electrodes carried out in 1976)

Dependence on electrical conductivity
There is a minimum conductivity of 200 µS/cm required. Increase of output signal to 100 µS/cm: 4%.
Further increase of output signal to 3000 µS/cm: 5%
If the operating range is around or above 1000 µS/cm a recalibration at a conductivity value of approximately 1000 µS/cm is recommended, whereby it must be noted, that the small influence due to conductivity becomes less significant above 1000 µS/cm.

Dependence on pH-value
The zinc electrode type is applicable in the range of pH 6.5–9.
The iron electrode type in the range of pH 6–9.
Decrease of output signal from pH 7–pH 8 4%
Increase of output signal from pH 7–pH 6.5 3%

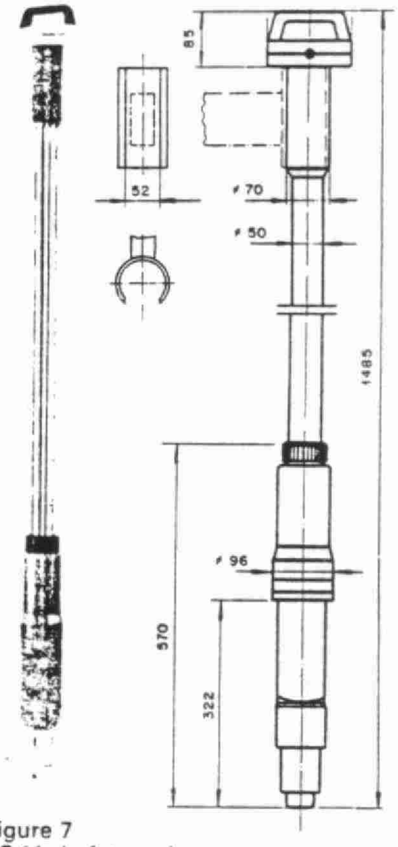


Figure 7
SS 11 shaft type, in open bracket, dimensions in mm, fig. 8

9. Advice for the installation of the Züllig d.o. probe
The probe is best mounted in a location which would give a reasonably representative water sample. For this purpose, we supply a variety of probe brackets.
The electrode has to be submerged in the medium by 0.5–1.5 m. Strong water currents should be avoided. For plug-in connection of the probe near the measuring location, we recommend to use the watherproof field mounting socket type FA-RAE4. As measuring cable, for the connection of the probe to the socket or to the transmitter, we recommend a special cable containing three twisted pairs of wires $3 \times 2 \times 1$ mm².

10. Electrical data
See data sheet DO-30

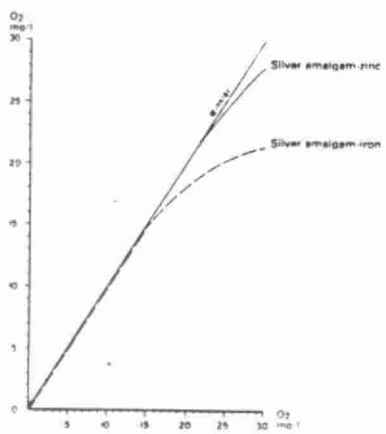


Figure 10
Linearity of the operating ranges of the electrodes

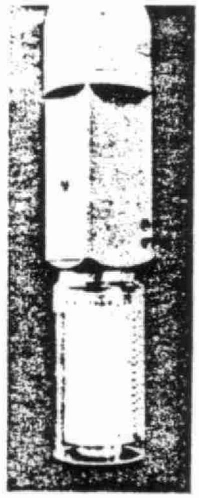


Figure 9
Cylinder type K_2 for protection against high current and bulky solid matter

EMERGING WATER SUPPLY TECHNOLOGY

AWWARF Code #: SW-05

PROJECT DESCRIPTION

Project Title:

Project "AQUA PURA"
Facility for Packing and Dispatch of
Emergency Water in Zurich

Contact (name of person, organization, address, telephone):

Maarten Schalekamp, Dr. sc.tech. h.c. ETH
Director Water Supply Zurich
and
Armin Näf, Vice-Director

CH-8023 ZURICH, Switzerland. Telephone: 01/435 21 11

Project Description (Please attach a schematic diagram if appropriate):

1. General

The concept of Zurich's Emergency Water Supply forsees that the inhabitants will supply themselves during the first few days after a catastrophy with drinking-water stored in their homes.
However, the recommended provisions for an emergency are not followed very seriously. The (mineral) water in one litre bottles, available everywhere, is accepted very reluctantly on practical grounds (heavy, fragile glass containers, limited stacking).
The previous and current contribution of the Water Supply Zurich to further the drinking-water emergency storage, is the supply of emergency water-plastic bags, Type Bertopack, containing one litre of treated lake-water. Unfortunately, the taste of the water in this packing is impaired and the bags become permeable.

2. Project Description

The following objectives should be obtained:

- solution of the quality problem
- solution of the question of distribution by packing for the wholesale trade and for the WSZ-own use
- substitution of the existing packing facility.

Of the current three projects which are under consideration, the project "Felsenquelle aus Kohlboden" (best springwater of the WSZ-springs in the Lorze valley), is primarily being studied. The bottling would take place in a bottling and dispatching plant in the industrial zone at Sihlbrugg. A minimal amount of at least 4 g/l carbon dioxide will be added to the spring-water in order to make this emergency water suitable for daily use (renewal of emergency store).
Packing: With the new, environmentally-conducive synthetic material PET (Polyethylenterephthalate), a suitable packing material is now available. The most suitable bottle shape and unit size are currently under study. Questions of storage and quality have still to be settled by the project groups, partly by means of tests.

Operating and cost data (including data on efficiency, results, etc.):

Information about costs are not yet available.
Production about 4000 litres per hour.

Place(s) of installation/application (including dates):

a) in a rented hall in the industrial zone of Sihlbrugg (Canton of Zug) or
b) in the Lakewater Plants of Lengg or Moos of the Water Supply Zurich

Patent staus, if applicable:

none

Other information (e.g., funding source, cooperating agencies, etc.):

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

Wassernotvorrat im Keller

KARL DIETLICHER, Zürich

Es ist ein schlimmes Ding,
den Brunnen erst zu graben,
wenn der Durst den Schlund ergreift. Plautus

Kurzfassung

Das Notstandskonzept sieht in der ersten Phase den totalen Ausfall der Wasserlieferung vor und nimmt an, dass die Bevölkerung wegen einer Verseuchung der Luft bis zu 14 Tagen in den Schutzräumen verbleiben muss. In dieser Zeit ist jeder Einzelne auf seinen persönlichen Vorrat im privaten oder im öffentlichen Schutzraum angewiesen. Für die öffentlichen Schutzräume sind 50–70 l pro Person in festen Wassertanks geplant, die durch Chlorpräparate haltbar gemacht werden. Im privaten Schutzraum sind mindestens 10–20 l pro Person vorzusehen. Sie können als behelfsmässige Wasserreserve in Gefässen eingelagert werden oder als echte, bis drei Jahre haltbare Wasserkonserve in Form von kohlensäurehaltigem Mineralwasser. Als vorteilhafte Alternative bietet sich auch eine Dauerkonserve von aufbereitetem Seewasser an, das mit einer Zugabe von 0,1 mg Silber/l für mindestens fünf Jahre haltbar gemacht wird. Das Wasser wird mit einer Waterline Abpackmaschine in äusserst platzsparende und stabile Kunststoffsäcke abgefüllt.

* Bisherige Praxis WV Zürich seit 1975

Practice of Zurich Water Supply since 1975

pendant de sa réserve personnelle, que ce soit dans les abris privés ou publics. Pour les abris publics, ce sont, par personne, 50–70 litres d'eau potable traitée au chlore pour sa conservation qui sont prévus en réserve dans des réservoirs fixes. Dans les abris privés, il faut prévoir au minimum 10–20 litres par personne. Il peut s'agir de réserves improvisées d'eau ordinaire dans des récipients ou bien de vraies conserves d'eaux minérales contenant des gaz carboniques, qui peuvent être gardées pendant trois ans. Comme autre alternative intéressante, on peut utiliser des conserves durables d'eau de lac, traitée avec une adjonction de 0,1 mg d'argent par litre et qui ainsi se conserve au moins pendant cinq ans. Ces réserves sont contenues dans des sacs en plastique, stables et peu encombrants, remplis par une machine à empaqueter en continu.

Abstract

The emergency concept foresees in the first phase the total breakdown of the water supply and assumes, that the population, because of a contamination of the air, will have to remain up to 14 days in the shelters. During this time each person is dependent on his personal water store in the private or public shelters. It is planned to provide in rigid water tanks 50–70 litres per person which is preserved by the addition of chlorine preparations.

In private shelters at least 10–20 litres per person should be available. The water can be stored as a temporary reserve in various containers or as proper water preserve in form of carbon dioxide containing mineral water which can be kept up to three years. As an advantageous alternative, a permanent preserve of treated lakewater is available, which has been dosed with 0.1 mg silver per litre and which will keep for at least five years. The water is packed into space-saving, sturdy plastic bags by a special packing machine.

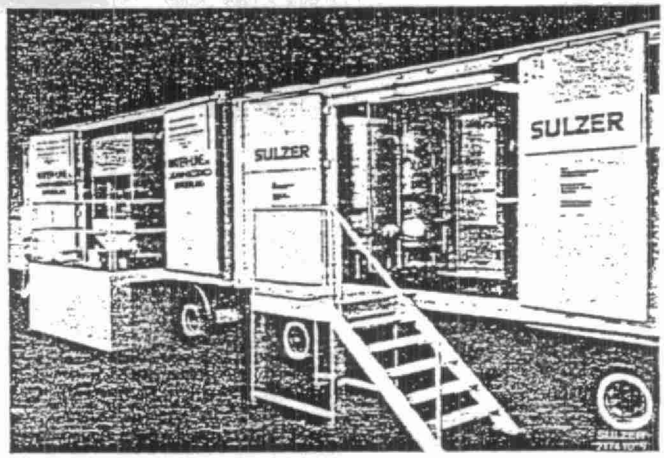


Abb. 4 Mobile Wasseraufbereitungs- und Abfüllanlage «Sulzer-Waterline».

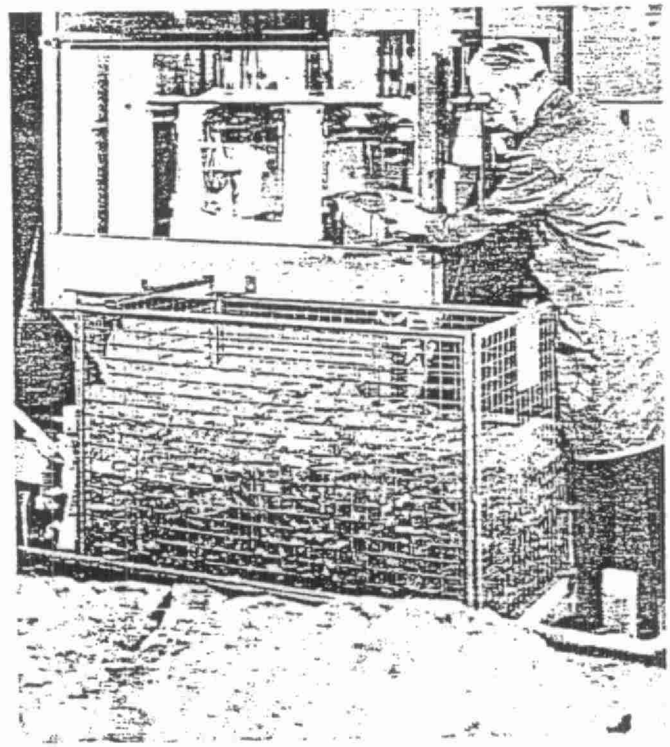


Abb. 5 Abfüllen der Notwasserbeutel im Werk Lengg.

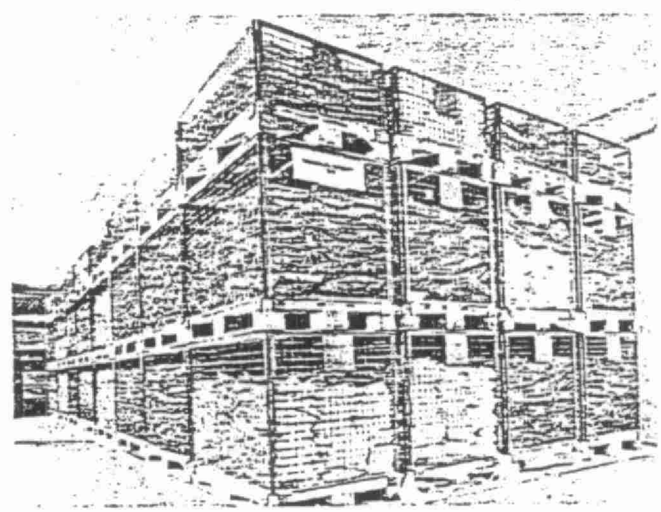


Abb. 6 Lager mit Notwasserbeuteln in Containern (Gemeinde Zollikon).

(published in "Gas Water Wastewater" No.9/198
by Swiss Gas and Water Industry Association,
Zurich)

 AWWARF Code #: SW-06

PROJECT DESCRIPTION

Project Title:

The Layered Upflow Carbon Adsorption (LUCA) for the Removal of Trace Organic Contaminants

Contact (name of person, organization, address, telephone):

Christoph Munz & Markus Boller - Swiss Federal Institute for Water Resources and Water Pollution Control (EAWAG), 8600 Dubendorf, Switzerland

Jean-Louis Walther and Ralph Bland - Hofmann, Robadey et Walther SA, Pre Tavanne 4, 2900 Porrentruy, Switzerland

Project Description (Please attach a schematic diagram if appropriate):

The natural organic matter found in virtually all drinking water sources is typically present at much higher concentrations than trace organic contaminants, such as chlorinated hydrocarbons. The heterogeneous matrix comprising the background organics is usually quantified by the dissolved organic carbon (DOC). The DOC is also less strongly adsorbed onto activated carbon (AC) than most chlorinated organics. Accordingly, in a fixed-bed adsorber the DOC front will move faster than that of the chlorinated organics. Hence, in a fixed-bed adsorber the activated carbon will become increasingly preloaded with DOC with increasing filter depth. This, in turn, will accelerate the breakthrough of the chlorinated organics and significantly reduce the life of the carbon. In addition to competitive adsorption interactions, it is therefore also necessary to consider the effects of DOC preadsorption on the AC when designing AC adsorbers.

In this study the Layered Upflow Carbon Adsorption (LUCA) filtration was investigated on a pilot plant scale as a potential mode of operation to reduce the preadsorption of DOC in AC adsorbers. In Porrentruy (Switzerland), two such adsorbers were run in parallel with two other fixed-bed adsorbers, one in the upflow and one in the downflow mode of operation. The pretreated water source (a natural spring) used in this investigation is contaminated with relatively low concentrations of trichloroethene (TRI) and tetrachloroethene (PER).

The results clearly show that the DOC preloading effect increases with increasing adsorber depth or empty bed contact time (EBCT). The usable AC adsorption capacity for trichloroethene at a bed depth of approximately 2 m in a fixed-bed adsorber is reduced by

almost an order of magnitude compared to the corresponding single solute isotherm. Approximately one half of this reduction is caused by competitive adsorption interactions, while the other half is due to the preadsorption of DOC on the AC. Also internal mass transfer processes are adversely and significantly affected by the preadsorption of DOC.
At Porrentruy, approximately 40% to 50% more bed volumes can be treated with the AC layered upflow filtration (15 m/h, 1.5 m total bed depth, and a target effluent concentration of 5 µg/l total chlorinated hydrocarbons) than with the fixed-bed adsorbers under similar operating conditions. This will result in approximately proportional cost savings for the regeneration of the granular activated carbon (GAC). Still superior performances can be expected for larger total bed depths.

Place(s) of installation/application (including dates):

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

UNITED KINGDOM

UNITED KINGDOM

EMERGING WATER SUPPLY TECHNOLOGY AWWARF Code #: UK-01

PROJECT DESCRIPTION

Project Title:

An Automatic Instrument to Measure Discolouration

Contact (name of person, organization, address, telephone):

Mrs. S M Williams
WRc Engineering
P.O. Box 85
Swindon, Wiltshire
UK
(0793) 511711

Project Description (Please attach a schematic diagram if appropriate):

Discoloured water is a major cause of consumer dissatisfaction with water supply. The customary method of measuring the extent of the problem has been to undertake chemical analysis of samples of water taken from various points along the distribution system.

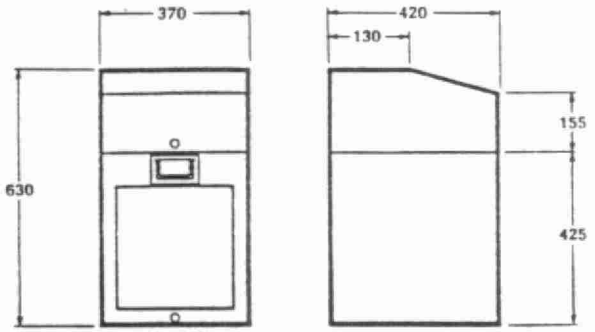
An instrument, the Automatic Liquid Filtration Instrument (ALFI) has been developed to automatically take up to 24 water samples at pre-set intervals (between 1 to 6 hours) and filter them, leaving any particulate matter present in the water on the filter paper. The colour of the filter paper can be compared with standards to yield a measure of discolouration. If required, bottled samples of filtrate or unfiltered water can also be collected. The instrument can filter the water that has been standing in the service pipe or it can be programmed to flush the service pipe to enable water representative of the quality in the mains to be collected. This allows a distinction to be made between problems arising from the domestic plumbing and those arising from elsewhere in the distribution system.

ALFI is battery-operated (using a built-in rechargeable battery), and is designed to be attached to a consumer's outside tap. It can be preprogrammed anytime up to seven days before it is required to start sampling.

Applications for ALFI include:-

- defining the frequency, duration and severity of discolouration incidents,
- investigating the cause of discoloured water problems,
- monitoring the quality of treated water,
- monitoring the effects of controlled operational changes (eg valving or rezoning), and monitoring the effectiveness of remedial measures for discolouration problems (eg relining, air scouring and silicate or polyphosphate dosing).

Operating and cost data (including data on efficiency, results, etc.):



All dimensions in millimetres

Minimum pressure 1.5 bar
Maximum pressure 20.0 bar
Weight 26 kg

Operating temperature 0 to 40

ALFI requires a water supply pressure of at least 1.5 bar and an adjacent drainage point NOT MORE THAN 30 cm above the base of the instrument. ALFI will usually be installed at an outside tap eg in a garage or conservatory. It is possible to install ALFI at a sink or basin provided that the waste water can drain away easily.

Place(s) of installation/application (including dates):

Patent staus, if applicable:

British and European patent obtained.

European No. 85307061.3 British 8424798

Other information (e.g., funding source, cooperating agencies, etc.):

ALFI was developed and patented by the Water Research Centre and is manufactured and marketed by Caradon Mira, Walker Crossweller and Co. Ltd., Whaddon Works, Cheltenham, Glos, GL52 5EP.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

A matter of discolouration

Dr Terry Winnington, advanced projects manager with the research and engineering department of Walker Crosweller & Co Ltd looks at important improvements in the measurement of water discolouration made possible by a new programmable filtration instrument.

IDENTIFYING and controlling problems with the quality of potable water calls for extensive monitoring exercises by water undertakings. This problem has become more acute as distribution systems have aged — it is reckoned that of the nation's 320,000km network (which would stretch eight times around the world), 50% is over 40 years old, some more than 100 years old. Over 80% is iron pipework subject to corrosion and liable to cause water discolouration problems.

After extensive studies over a 5-year period by the Water Research Centre, and development work carried out in conjunction with Walker Crosweller & Co Ltd, a new automatic instrument is now available which is designed to provide valuable improvements in field testing for the major water quality problem — discolouration.

Claimed to be capable of being programmed to operate at different time intervals without the need for an operator to be in attendance, it will give a direct indication at a glance of whether discolouration is occurring. Examination of the results will reveal the times when discolouration occurs, the degree of the problem and provide, where required, measured water samples for detailed laboratory analysis.

The instrument is known as ALFI — automatic liquid filtration instrument — and works on the principle of filtering a set volume of water. The colour on the filter paper can be compared with a standard colour and thus a measure of the discolouration can be obtained and recorded.

Supplying water that is safe to drink is the primary concern of a water undertaking but complaints understandably arise from consumers whose water supply shows problems of, for example, discolouration, unusual taste or odour.

In dealing with these problems, deteriorating pipework is not the only possible cause that may be found. Inadequate treatment and the disturbance of deposits are among other factors?

Identifying discolouration problems and their cause requires carefully planned and intensive sampling programmes. Times of sampling have to be varied to take into account variations in the quality of water as consumer demand and flow patterns change.

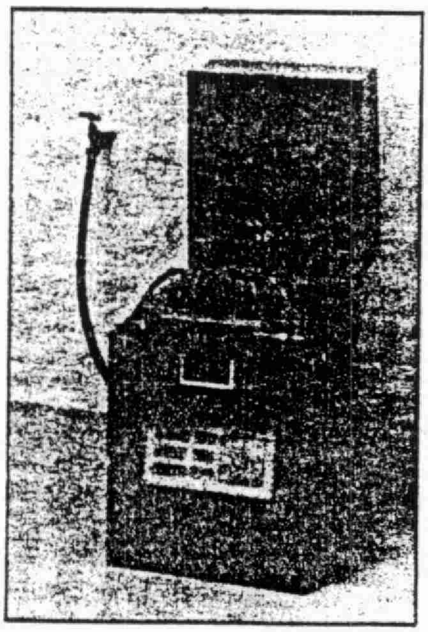
The Water Research Centre for some years investigated discolouration problems and has shown that filtration techniques are not only easier but for many purposes more relevant than laboratory analysis. The parameters currently used to determine whether discoloured water has occurred are chemical parameters such as iron, aluminium and manganese content. No evidence exists that high concentrations of these imply discoloured water problems. There was consequently a need for a parameter that determined discoloured water problems as perceived by the consumer.

It was apparent also that there was a need for a programmable automatic instrument capable of checking water quality at fixed time intervals for known volumes of flow.

Field trials showed the additional value of being able to link up to an external trigger source such as a turbidity meter and of including in the equipment the ability to take bottled samples, either filtered or unfiltered, to aid a detailed analysis.

Water scientists and engineers will now be able to use ALFI to perform the following specific functions:

1 define the frequency, duration and severity of discolouration;
2 investigate the cause of the problem;
3 monitor the effects of controlled operational changes such as valving and rezoning;
4 study specific persistent consumer complaints;
5 assess the effectiveness of remedial measures.



ALFI — the new automatic liquid filtration instrument.

The unit is programmed via an integral control panel, custom designed for ease of use and clarity of display. For example, the pre-set sampling interval ranging between 1 hour and 6 hours can be seen immediately and changed by a single button press. Controlled volumes of standing water can be purged from the supply and sample lines to ensure that the samples taken are representative of the water from the mains.

From the coupling on the mains water tap, the water enters the instrument through a 100 micrometre mesh strainer and a pressure regulating valve, factory set at 2 bar. Downstream of this a flow control valve restricts the maximum flow rate to 4.7 litres a minute.

On sampling, the water passes into the distribution manifold and through to one of 24 sampling locations. A sheet of filter paper covering all the sample positions will collect any particles greater than 1.2 micrometres on a 25mm diameter area and these will cause discolouration of the paper. On inspection, the filter paper gives an instant indication of the existence of discolouration and when compared with a standard colour chart gives an immediate measure of its severity.

A different shade of colour can often be indicative of a different cause of discolouration and the variation in filter colour grades can also indicate whether a problem is spasmodic or constant.

If it is necessary to know the concentration of metals in the water or the ratio of total to dissolved metals this can be achieved using a filter sheet with alternative sample positions punched out. Bottles would be inserted under the filter positions to collect both filtered and unfiltered water samples.

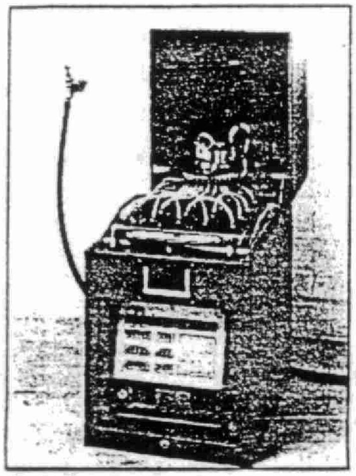
Where discolouration that occurs very infrequently is being examined, ALFI can be set to pass up to six samples through each filter point. In the case of severe, but infrequent discolouration, the facility has been incorporated for operation to be triggered from a turbidity meter with the precise sample times and volumes being logged for subsequent interrogation via a liquid crystal display.

With no filter paper inserted unfiltered samples can be collected for detailed analysis. From the filter paper the water passes either into a 150 millilitre sample bottles or to a drain outlet.

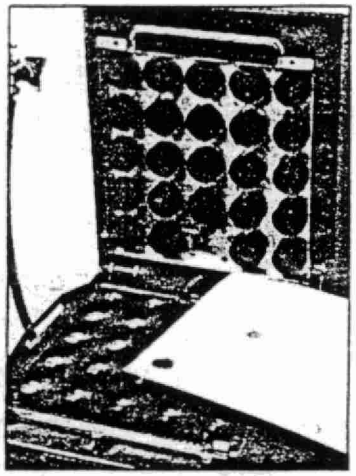
One of the first customers for ALFI is Severn Trent Water Authority which has ordered 50 units. They will be put to work on the 38,000km of mains pipework in the Authority's care, 80% of which is iron and some 60% unlined. Funds needed for renewal of this network will rise significantly over the coming five years.

For further information contact Caradon Mira Limited (previously Walker Crosweller). Tel: 0242 516317

Discoloured water problems solved?



ALFI fitted in consumer's home



...samples and analyses water

A new instrument developed by the Water Research centre to investigate and, it is hoped, solve the problem of discoloured water is being made and marketed by Arkon Instruments.

The Automatic Liquid Filtration Instrument (ALFI) is battery operated and can be installed in the consumer's home – on garden or garage tap – or in the distribution system. It can be automatically programmed to filter water and show at a glance the level of discolouration. It can also collect water samples for analysis to determine the cause of the problem.

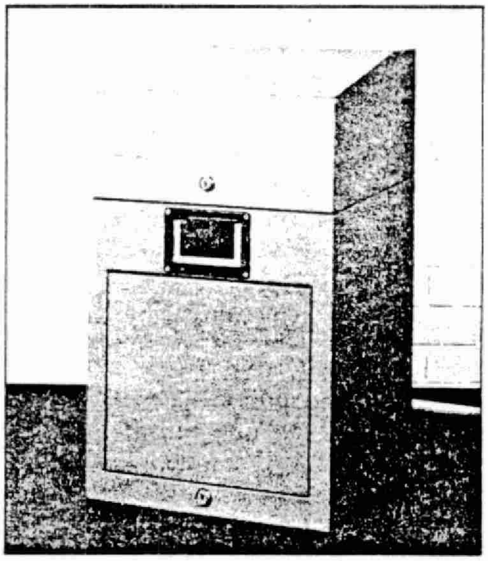
ALFI is designed to take a sample of water and filter it at programmed intervals, leaving the coloured particles on the filter paper. The colour of the paper can be calibrated against a standard colour chart to give a measure of discolouration. Pre-programming takes account of variations in quality of the water supply.

An important additional option where the incidence of discolouration is infrequent or severe is said to be the linking of the instrument to an external source, such as a turbidity monitor, which triggers the filtering and sampling operation automatically at the precise time the discolouration occurs.

In addition to enabling water industry scientists and engineers to investigate the causes of discoloured water and define the frequency, duration and severity of them, use of ALFI, it is claimed, will also enable them to monitor effects of controlled operational changes, to investigate specific persistent consumer complaints and to monitor the effectiveness of remedial and palliative measures.

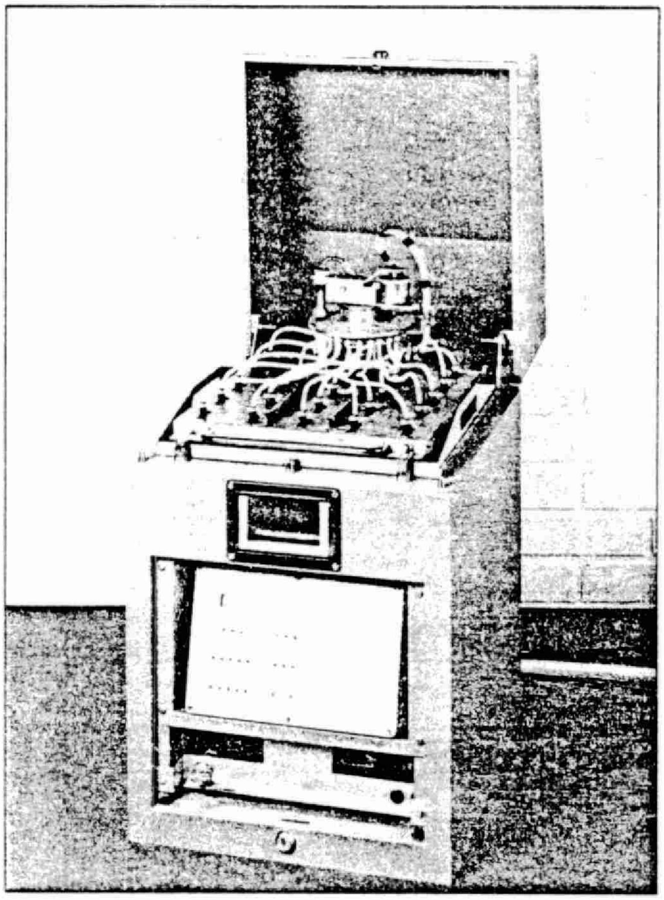
Details from Arkon Instruments, Unit KL3, Kingsville Road, Kingsditch Trading Estate, Cheltenham GL51 5PL.

Automatic Liquid Filtration Instrument (ALFI)



The problem associated with discoloured water resulting from corrosion in cast iron pipes and the need to automatically take water samples and filter them is well defined in the Manual for Rehabilitation of Water Mains published by WRC.

The ALFI was developed jointly by WRC and Walker Crosweller from an original WRC specification to automate previously labour intensive sampling techniques to provide an accurate and cost effective method for determining water discoloration caused by suspended particulate matter.



Applications

Water scientists and engineers will be able to use the instrument to combine several specific tasks:

- defining the frequency, duration and severity of discoloration
- investigating the cause of discoloured water problems
- monitoring the effects of controlled operational changes (eg valving and re-zoning)
- investigating specific persistent consumer complaints
- monitoring the effectiveness of remedial and palliative measures for discoloration problems (eg relining. air scouring and silicate and polyphosphate dosing).

Operation

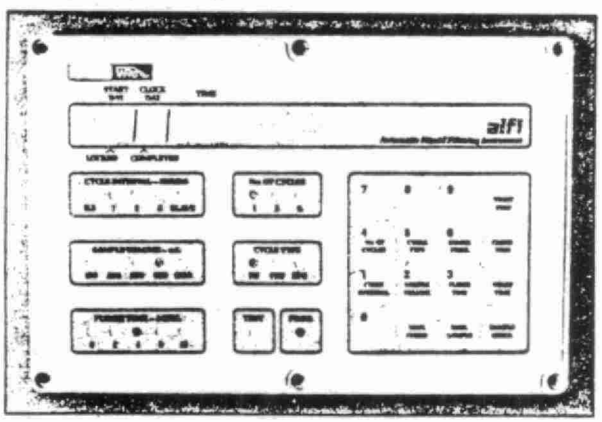
The ALFI is a transportable battery operated microprocessor-based instrument that can be programmed to take 24 water samples at intervals between ½ to 8 hours leaving any particulate matter on a filter paper. The colours of each sample can be compared with a standard chart to measure the discoloration. For applications where these effects are very infrequent the ALFI can be set to pass up to six samples through each of the 24 filter sample points.

In addition it can be programmed/set to take up to 24 unfiltered water samples in discrete bottles or any combination of filter or 100 ml bottle samples on the same cycle to allow detailed analysis of contaminated water.

Where discoloration is severe and infrequent, the ALFI can operate from an external turbidity monitor, with precise sample times and volumes being logged for interrogation via the liquid crystal display (LCD).

The ALFI may also be set to purge supply and sample lines of standing water to ensure that only valid samples are taken. To accommodate the variety of samples taken, there are three different sample purge cycles.

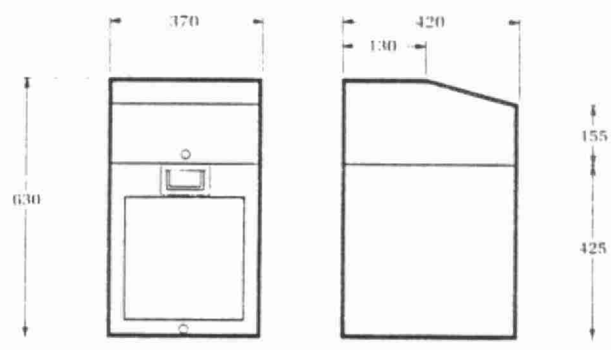
Programming



Sampling programmes are easily entered using the integral membrane keypad, liquid crystal display and LEDs. Security codes for access and programme locking can be used to prevent unauthorised use of the ALFI.

Technical Data

Enclosure	Transportable, all weather Weight 55lbs (without bottles)
Electronics	
Enclosure	IP.67
Microprocessor	6303 CMOS microprocessor A battery backed Real Time Clock retains all data for 48 hours with unit switched off
Keypad	16 pad tactile membrane
LCD	8 digit display
Battery	Rechargeable 15 amp hour fully sealed lead acid battery (30 days duration)
Sample bottles	150 ml
Filter paper	GF/C 1.2μm retention
Environmental	Operating temperatures between −5°C to +55°C



All dimensions in millimetres

PROJECT DESCRIPTION

Project Title:

Water Works Sludge Treatment

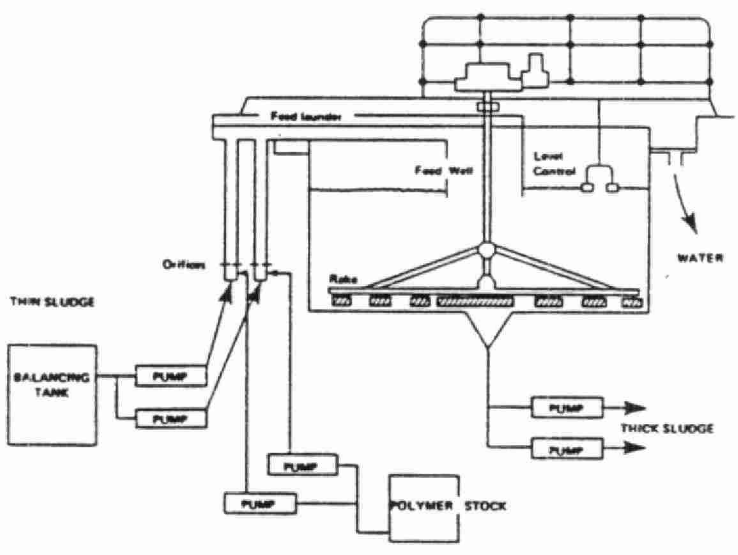
Contact (name of person, organization, address, telephone):

Mr. J. Warden
WRc Processes
Elder Way
Stevenage UK

Tel: (0438) 312444

Project Description (Please attach a schematic diagram if appropriate):

Sludge is produced by all water treatment plants which use alum or ferric salts in the production of drinking water. The volume of sludge can be as high as 6% of the water treated and it is of no agricultural value and is expensive to dump. Following research and field work WRc has developed a design procedure for specifying thickening plant without the need to carry out extensive trials. All that is required is a sample of the raw water.



Polymer thickening of a waterworks coagulant sludge begins with withdrawal of sludge from an agitated balancing tank of sufficient capacity to buffer variations in flow and concentration of the various works effluents. The sludge is deflocculated by pumping at constant rate through a fixed orifice while the required dose of polymer is injected. The feed pump/dosing pump/orifice plate combination is a constant-flow system. Long-term variations in flow are handled on a

Project Description - continued

small unit by operating for a variable period in each day; on a large works by switching feed sets on an off as required. After flocculation, gentle shear assists aggregation of the flocs but turbulence at pipe fittings and free fall-out of pipe ends must be avoided. Therefore the dosing point is preferably close to the thickener and the flocs are floated into the feedwell along an open launder lying in the water surface. The attendant will look into the launder to note the condition of the flocs and take any remedial action that may be required.

Operating and cost data (including data on efficiency, results, etc.):

The WRc water works sludge system is simple, cheap and reliable. The sludge is concentrated into a thick paste in a continuous thickener. It can then be disposed of in this form or easily processed in a filter press to produce a solid cake. All coagulants wastes can be converted into thick sludge ranging from 6% to 25% solids. The degree of thickening depends on raw water quality, not on the waste concentration, which usually ranges from 0.3 to 4.0 g/l. The capital cost of the system is 30% less than conventional systems and savings so far in the UK have exceeded £3.25M. Over 30 water treatment plants in the UK have been modified to use the new technology.

Place(s) of installation/application (including dates):

List of some major works using the WRc technology:-
Font burn. England. Northumbrian Water 16Ml/d 1984
Headley Park. England. Mid Southern Water Co 7Ml/d 1980
Barconbe Mills. England. Mid Sussex Water Co 22Ml/d 1981
Prewley. England. South West Water 17Ml/d 1982
Huntingdon. England. North West Water 360Ml/d 1982
Bough Beach. England. East Surrey Water Co 45Ml/d 1982
Horsley. England. Newcastle and Gateshead Water Co 113Ml/d 1982
Ballymore Eustace. Eire. Dublin Corporation 200 Ml/d 1984
Langsatt. England. Yorkshire Water 60Ml/d 1985
Rosebury. Scotland. Lothian Regional Council 32Ml/d 1987

Patent staus, if applicable:

No patents but WRc is in possession of considerable know how.

Other information (e.g., funding source, cooperating agencies, etc.):

The research programme was carried out by WRc on behalf of the UK water undertakings. The technology has been very successful in the United Kingdom and has won a Pollution Abatement Award. Interest is now being shown outside the UK and plant designed in accordance with the WRc method has been constructed in Eire, New Zealand and the United States. Research work is currently in hand to study the biological processes that take place in the sludge and their contribution to taste problems.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

UNITED STATES

UNITED STATES

EMERGING WATER SUPPLY TECHNOLOGY AWWARF Code #: US-01

PROJECT DESCRIPTION

Project Title:

Rapid Detection Method for Coliform Bacteria and *Escherichia coli* in Drinking Water

Contact (name of person, organization, address, telephone):

Stephen C. Edberg, Ph.D., A.B.M.M.
Director, Clinical Microbiology Laboratory
School of Medicine
Yale University, New Haven, CT 06510
(203) 785-2457

Project Description (Please attach a schematic diagram if appropriate):

The project was a national evaluation of a rapid detection method ("colilert") for the simultaneous detection and specific identification of total coliforms and *E. coli* in drinking water.

Colilert is a formulation of salts, nitrogen, and carbon sources that are specific only to total coliforms. It provides specific indicator nutrients ONPG (O-Nitrophenyl-B-d-Galactopyranoside) and MUG (4-Methylumbelliferyl-B-d-Glucuronide) for the target microbes, total coliforms, and *E. coli*. As these nutrients are metabolized, yellow color (from ONPG) and fluorescence (from MUG) are released confirming the presence of total coliforms and *E. coli*, respectively (see photographs). Non-coliform bacteria (heterotrophic plate count organisms) are chemically suppressed and cannot metabolize the indicator nutrients. Consequently, they do not interfere with the specific identification of the target microbes.

Total Coliforms and *E. coli* are specifically and simultaneously detected and identified at 1 CFU/100 ml of sample, in 24 hours or less, by inoculating the media with the water sample. No further sample manipulation or testing is required.

Operating and cost data (including data on efficiency, results, etc.):

Results from the field trials showed:

- Sensitivity to a bacterial concentration of 1 CFU/100 mL
- Results in a maximum of 24 hours, most in the 16-18 hour range (see attached statistical comparison between standard methods MPN and Colilert MPN)
- Simultaneous detection and identification of Total Coliforms and *E. coli*
- The dry formulation requires no refrigeration and has a long shelf life
- Autoanalytical nature was confirmed, after inoculation of the water sample no further tests need be done
- It can be configured in either a Presence/Absence test or MPN
- Can be used equally well by small and large utilities
- Cost is less than current procedures
- Specific for the target microbes
- No HPC interference with the test results

Furthermore, the following advantages over current methods were found during the study:

- Constancy of medium formulation throughout the study and across the nation
- No preparation of media
- Ease of reading the results permits even the small utility to perform the test
- The procedure is considerably easier to perform than either MPN or MF by Standard Methods
- Reading of the result of the test is definite and not susceptible to subjective interpretation
- Has the potential to be instrumented and automated

Place(s) of installation/application (including dates):

Field Trials conducted at:

California-American Water Co., Monterey, CA (groundwater, reservoirs)
Washington State Laboratory, Seattle, WA
West Penn Water Co., Pittsburgh, PA (surface)
Cincinnati Water Works, Cincinnati, OH (surface)
North Andover, MA Water Dept. (surface or ground)
South Central Connecticut Regional Water Authority, New Haven, CT (surface)
Cobb County-Marietta Water, Marietta, GA
Monmouth WAter Co., Monmouth, NJ (surface and ground)
New York City Water Dept (surface)
Bridgeport Hydraulic Co., Bridgeport, CT (surface)

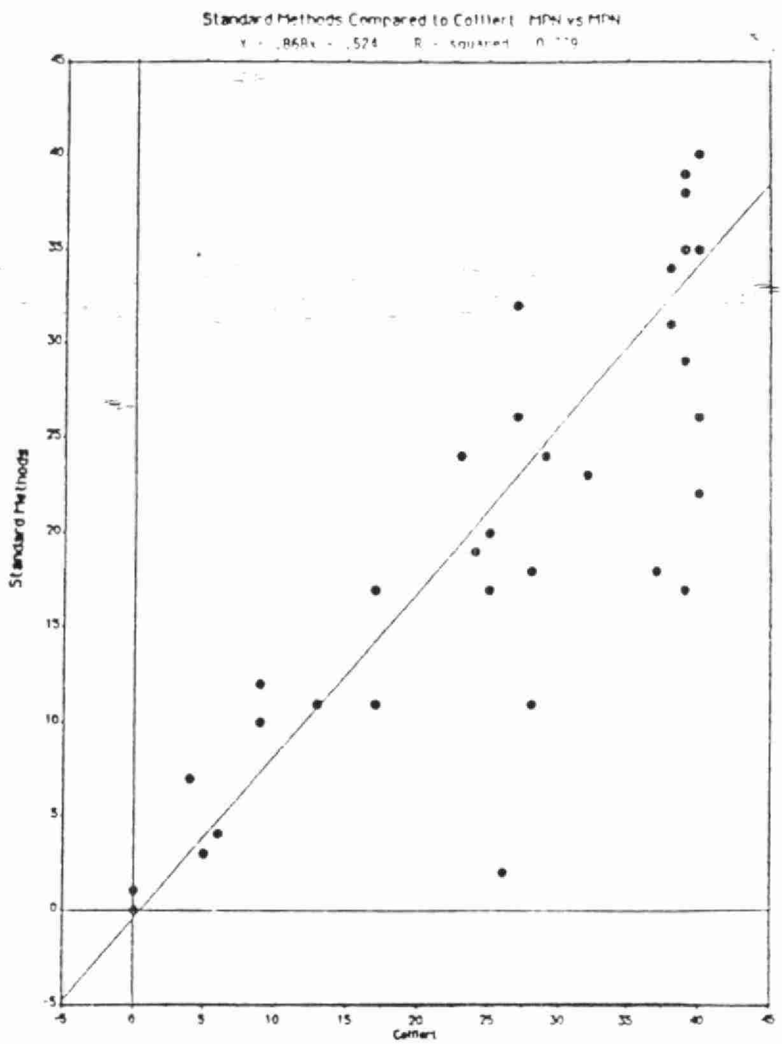
Patent staus, if applicable:

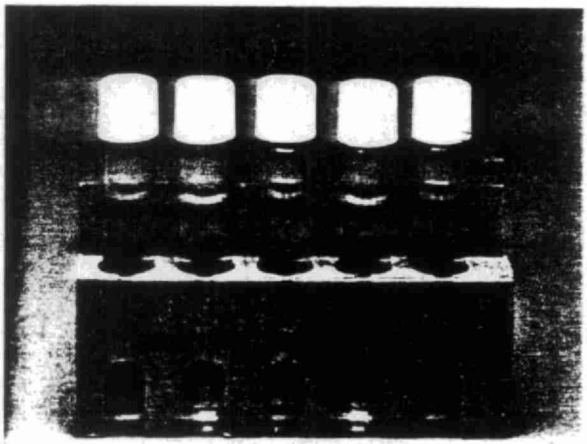
"Colilert" is a trademark name; media formulation non-proprietary.

Other information (e.g., funding source, cooperating agencies, etc.):

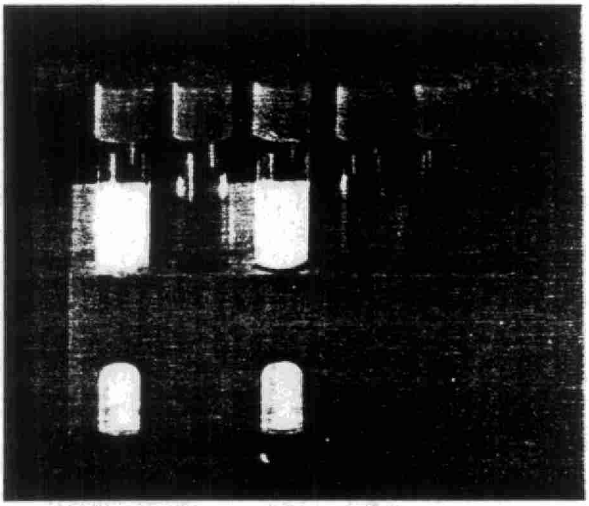
Project jointly funded by AWWARF and U.S. EPA; application made to U.S. EPA for approval of "Colilert" as an equivalent method to either MPN or MF Standard Methods.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.





Photograph A
Colilert Multiple Tube Format after 24-hour incubation at 35°C. Tubes 1, 3, and 5 are positive for coliforms (yellow color).



Photograph B
Same Multiple Tube Format as in Photo A. Tubes 1 and 3 are positive for *E. coli* (fluorescence) while tube 5 is negative for *E. coli* (no fluorescence).

EMERGING WATER SUPPLY TECHNOLOGY AWWARF Code #: US-02

PROJECT DESCRIPTION

Project Title:

Polymeric Inorganic Coagulants

Contact (name of person, organization, address, telephone):

Dr. Charles O'Melia
The Johns Hopkins University
Charles & 34th Streets
Baltimore, MD 21218
Telephone: (301) 338-7102

Project Description (Please attach a schematic diagram if appropriate):

Aluminum and iron(III) salts are common conventional coagulants in potable water treatment. They have come into widespread use because of their effectiveness and their cost. The solution chemistry of aluminum and iron(III) and their reactions with turbidity and color have been studied extensively and some clarification of their properties and applications has been achieved. A recent focus in potable water treatment has been the preparation and use of preformed "polymeric" iron(III) and aluminum species as coagulants.* Advantages attributed to these inorganic polymeric coagulants include enhanced removal of color and turbidity, reduced solubility (for aluminum) at alkaline pHs, improved effectiveness at low temperatures, reduced dosage requirements, lowered sludge production, improved fluoride removal (for aluminum), and effectiveness in direct filtration. A concensus on the preparation, nature, and effectiveness of these materials has, however, not been established. Commercial preparations are becoming available in the United States, on site preparation may be feasible, and a study of these materials and their potential applications is timely.

The objectives of this research are (1) to determine appropriate conditions for the preparation of polymeric inorganic coagulants, (2) to identify the nature of these materials, and (3) to evaluate their applications in potable water treatment.

Operating and cost data (including data on efficiency, results, etc.):

Project is nearly completed. Final report expected Spring 1988.

Place(s) of installation/application (including dates):

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

EMERGING WATER SUPPLY TECHNOLOGY

AWWARF Code #: US-03

PROJECT DESCRIPTION

Project Title:

Production and Use of Polymerized Aluminum Species From Alum

Contact (name of person, organization, address, telephone):

Brian A. Dempsey, Principal Investigator
Pennsylvania State University
212 Sackett Building
University Park, PA 16802
814-865-1226

Project Description (Please attach a schematic diagram if appropriate):

The objectives of this research are to develop methods for the controlled polymerization of aluminum sulfate.

The independent variables will be temperature, dilution factor, hydroxyl ligand number and time.

Operating and cost data (including data on efficiency, results, etc.):

Projected savings of costs in lower doses and lower waste handling costs as a result.

Place(s) of installation/application (including dates):

Lab work - field verification planned.

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

EMERGING WATER SUPPLY TECHNOLOGY

AWWARF Code #: US-04

PROJECT DESCRIPTION

Project Title:

Development of Rapid Small Scale Adsorption Tests

Contact (name of person, organization, address, telephone):

John C. Crittenden, Ph.D., P.E.
Michigan Technological University
Civil Geology Building
College of Engineering
Dept. of Civil Engineering
Houghton, MI 49931
(906) 487-2798

Project Description (Please attach a schematic diagram if appropriate):

Increased attention to low levels of organic chemicals in drinking water has led to an increased need for their removal. Granular activated carbon (GAC) is an effective technique for oroganic chemical removal but it can be quite expensive, especially if it is improperly designed. Historically, proper design of GAC adsorbers has required expensive, time consuming pilot scale testing. This project is aimed at developing a rapid, small scale test to replace pilot scale testing.

The rapid small scale adsorption test (RSSCT) should be able to simulate months of pilot and/or full scale adsorber operation in several days without the development of expensive isotherm/benetic data. The RSSCT is a small scale physical model designed so that it gives identical performance to a full scale adsorber.

This project will determine the proper adsorbent particle size, hydraulic loading, empty bed contact time for RSSCTs to simulate full scale adsorbers. The project will examine dependence of surface diffusivity on particle size, develop scaling equators and verify these equations in comparing RSSCT results with pilot scale work.

Operating and cost data (including data on efficiency, results, etc.):

This project is ongoing and is still in the data gathering stage. Progress is being made but more work is required to determine the scaling equations and particle size/diffusivity relationship for various raw water qualities.

Place(s) of installation/application (including dates):

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

EMERGING WATER SUPPLY TECHNOLOGY AWWARF Code #: US-05

PROJECT DESCRIPTION

Project Title:

Trihalomethane Reduction By Enhanced Floc-blanket Clarification

Contact (name of person, organization, address, telephone):

Edwin Snyder
Manager of Operations
Dept. of Public Works
City of Newport News
36 Reservoir Rd.
Newport News, Virginia 23602
(804) 247-8545

or

E. Randall Hoffman
Project Manager
CH2M HILL
P.O. Box 4400
Reston, Virginia 22090
(703) 471-1441

Project Description (Please attach a schematic diagram if appropriate):

See Project Description on reverse side of this page.

The City of Newport News, Virginia is constructing a new 25 mgd water treatment plant which will be placed into operation in the summer of 1988. In planning the new Harwood's Mill plant, the City and it's consultant developed a goal-oriented strategy to meet current as well as potential future drinking water regulations which are in a dramatic state of flux.

A primary strategy was to incorporate the process flexibility to reduce the total trihalomethane (TTHM) content of the treated water to the extent that may be necessary under anticipated future EPA regulations, a range of .025 to .075 mg/l compared to the present standard of .10 mg/l. Floc-blanket clarification, using Infilco Degremont Inc.'s Superpulsator clarifier system, was selected as the primary clarification process. This process is well suited to treating the reservoir water which has a moderate-to-high color and TOC content. The floc-blanket process was also selected due to the anticipated flexibility to achieved enhanced TTHM reduction if necessary through (a) low pH coagulation, (b) addition of powdered activated carbon (PAC), and (c)pre-ozonation.

A 14-month, three-phased pilot study was conducted concurrent with the design development in part to evaluate the potential for enhanced TTHM reduction through use of the floc-blanket process with the variations noted above. Both PAC addition (approx. 25 mg/l) and preozonation (approx. 0.1 mg/mg TOC) were individually demonstrated to provide enhanced TTHM reduction, with maximum enhancement demonstrated with simultaneous dosage, in combination with coagulation at pH 6. Such enhance treatment appears capable of producing system TTHM values as low as .050 mg/l TTHM, whereas conventional treatment would result in near 0.10 mg/l TTHM. Use of granular activated carbon was evaluated as a means of achieving lower TTHM values, and was shown to be effective, particularly in combination with preozonation ahead of the carbon.

The initial plant construction will provide for enhanced floc-blanket clarification with low pH coagulation and PAC addition capabilities. In addition, provisions are included to readily incorporated ozonation and granular activated carbon treatment should such become necessary or desirable. The plant will include permanent pilot plant facilities for routine process optimization, as well as additional research regarding enhanced floc-blanket clarification and granular activated carbon.

The City has no current plans to apply for a patent for the enhanced floc-blanket processes.

EMERGING WATER SUPPLY TECHNOLOGY

AWWARF Code #: US-06

PROJECT DESCRIPTION

Project Title:

Flotation Studies of Low Turbidity Waters Containing Humic Substances and Algae

Contact (name of person, organization, address, telephone):

Kim R. Fox, Drinking Water Research Division, Water Enginering Research Laboratory, U.S. EPA, Cincinnati,OH 45268 (Tel (513) 569-7820

Project Description (Please attach a schematic diagram if appropriate):

This project will investigate dissolved air flotation (DAF) as a drinking water treatment method. The primary objectives of the study are (1) to examine DAF for the removal of particulates from water supplies and to compare its performance with conventional water treatment of coagulation-flocculation followed by gravity settling, and 2) to examine DAF for removal of organic matter including color, total organic carbon, trihalomethane precursors, and total organic halide precursors and to compare its performance with conventional treatment of coagulation flocculation followed by gravity settling.

The study approach involves laboratory studies (Phase I) with model raw waters and field related studies (Phase II) with actual water supplies. The types of waters selected for the study have been chosen so the results of the research will apply to water supplies with low turbidity, water supplies that contain natural color (humic substances), and water supplies with seasonal algal problems. The results of this research will be of interest to communities which need to build new water treatment plants and are seeking an economical alternative to conventional type water treatment.

Operating and cost data (including data on efficiency, results, etc.):

Data will be collected during the course of the probject to evaluate the effects of raw water quality (ie turbidity, particle counts, algal cell counts, and temperature) on dissolved air flotation. Various other operating parameters such as coagulant type and dosages, pH, recycle ratio, flocculation time, and pressure will also be evaluated.

Place(s) of installation/application (including dates):

University of Massachusetts
Amherts, Mass.
9/1/85 - 2/29/88

Patent staus, if applicable:

NONE

Other information (e.g., funding source, cooperating agencies, etc.):

Cooperative Agreement: U.S. EPA and University of Massachusetts
CR 812639

Principal Investigator: Dr. James K. Edzwald, Un. of Massachusetts

Project Officer: Kim R. Fox, U.S. EPA, WERL

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

EMERGING WATER SUPPLY TECHNOLOGY AWWARF Code #: US-07

PROJECT DESCRIPTION

Project Title:

VOC Destruction by Ozone/Hydrogen Peroxide Process

Contact (name of person, organization, address, telephone):

Dr. William H. Glaze
Environmental Science and Engineering Department
University of California, Los Angeles, CA 90024
(213) 206-1278

Project Description (Please attach a schematic diagram if appropriate):

Packed tower aeration (PTA) and granular activated carbon (GAC) have historically been utilized for control of volatile contaminants. In some locations, however, contaminant transfer to other media necessitate off gas control with PTA or special handling for spent GAC. In those locations, a destructive technology would be a desirable alternative. The application of ozone in conjunction with hydrogen peroxide has been found to be very effective for destruction of trichloroethylene (TCE) and tetrachloroethylene (PCE) in Los Angeles groundwater.

In laboratory and pilot studies, a 70 L stainless steel stirred tank reactor (attached Figures 4A and 4B) was utilized. It was fitted for ozone (O_3) feed, UV lamps, hydrogen peroxide (H_2O_2) feed, O_3 inlet and off gas monitoring and liquid sample collection. These advanced oxidation techniques employing oxidants and UV are designed to produce hydroxyl radical, a specie that will react readily with organic contaminants.

Operating and cost data (including data on efficiency, results, etc.):

See Attachment

Place(s) of installation/application (including dates):

bench scale: UCLA (see contact) October 1986-present
pilot scale: Los Angeles Dept. Water Power
(see funding below) May 1987-present

Patent staus, if applicable:

Not applicable

Other information (e.g., funding source, cooperating agencies, etc.):

funding: U.S.EPA, Drinking Water Research Division
Cincinnati, OH 45268
Richard J. Miltner (513)569-7403

Los Angeles Department of Water and Power
Los Angeles, CP 90051
Laurent McReynolds (213)431-4211

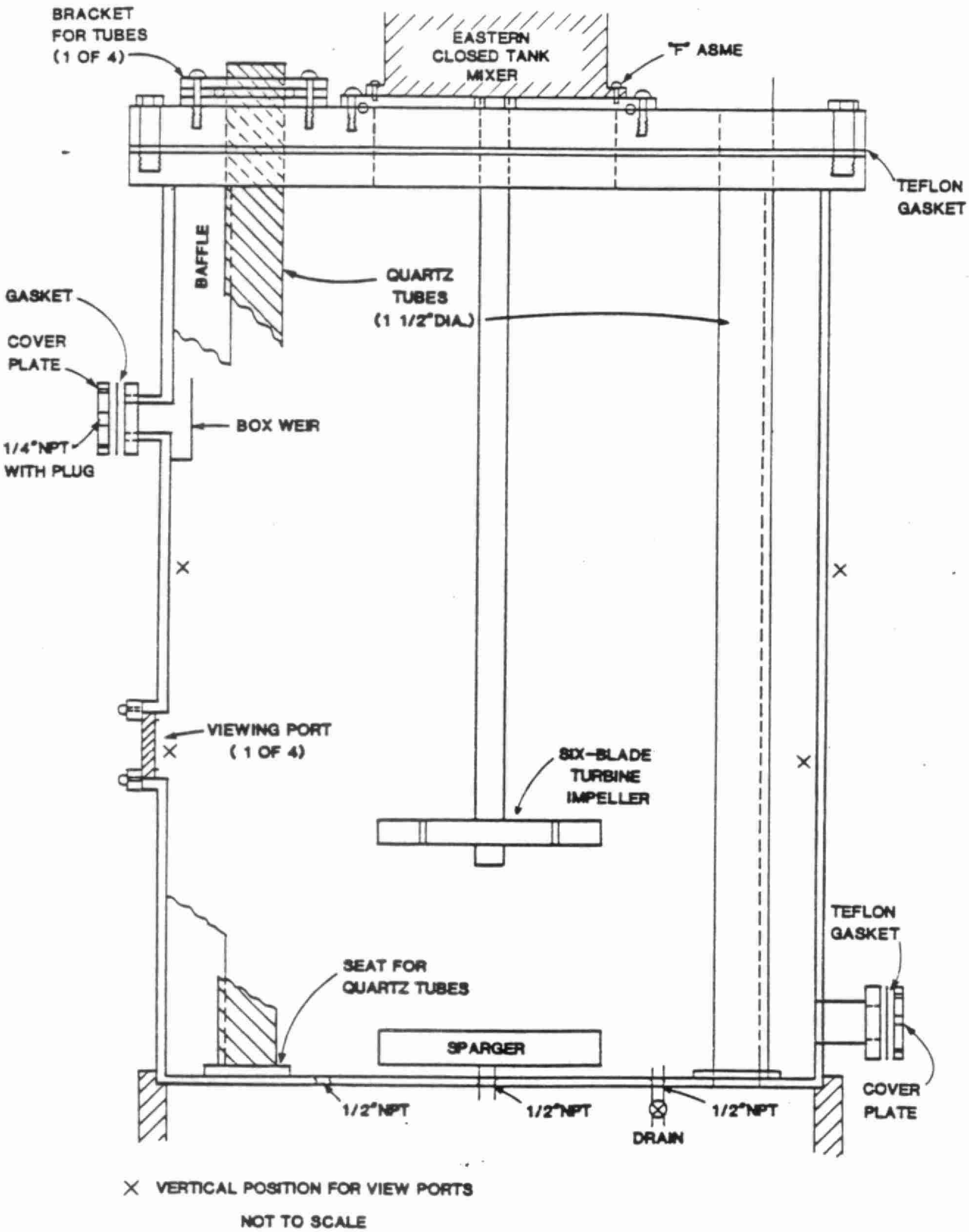
If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

Operating and Cost Data:

Los Angeles groundwater was treated in the apparatus described by O_3, UV, O_3/UV, O_3/H_2O_2 and H_2O_2/UV. Kinetic studies were conducted for each treatment scheme. O_3/H_2O_2 and O_3/UV were found to be the most effective schemes for control of TCE under the conditions studied. Kinetic data are plotted in Figures A-1 and B-1, respectively. These data indicate that for 90 and 99 per cent removal of TCE, 13 and 26 min min contact time respectively would be required for each of the two schemes at 5.4 mg/L (15 mg/min) O_3 dose. With ozone normalized at 5.4 mg/L, the advantage of peroxide is evident. For 99 per cent removal of TCE, 5.4 mg/L H_2O_2 would be required in the O_3/H_2O_2 scheme, whereas 0.57 watts/L would be required in the O_3/U V scheme. Comparing projected costs for both H_2O_2 chemical and power for UV lamps at $0.06/kwhr, a 35 per cent cost savings results with the selection of H_2O_2, i.e., $0.035 vs. $0.054/1000 gallons at 1.0 mgd. Total costs of O_3/H_2O_2 are anticipated to compare favorably with GAC and with PTA utilizing GAC off gas control.

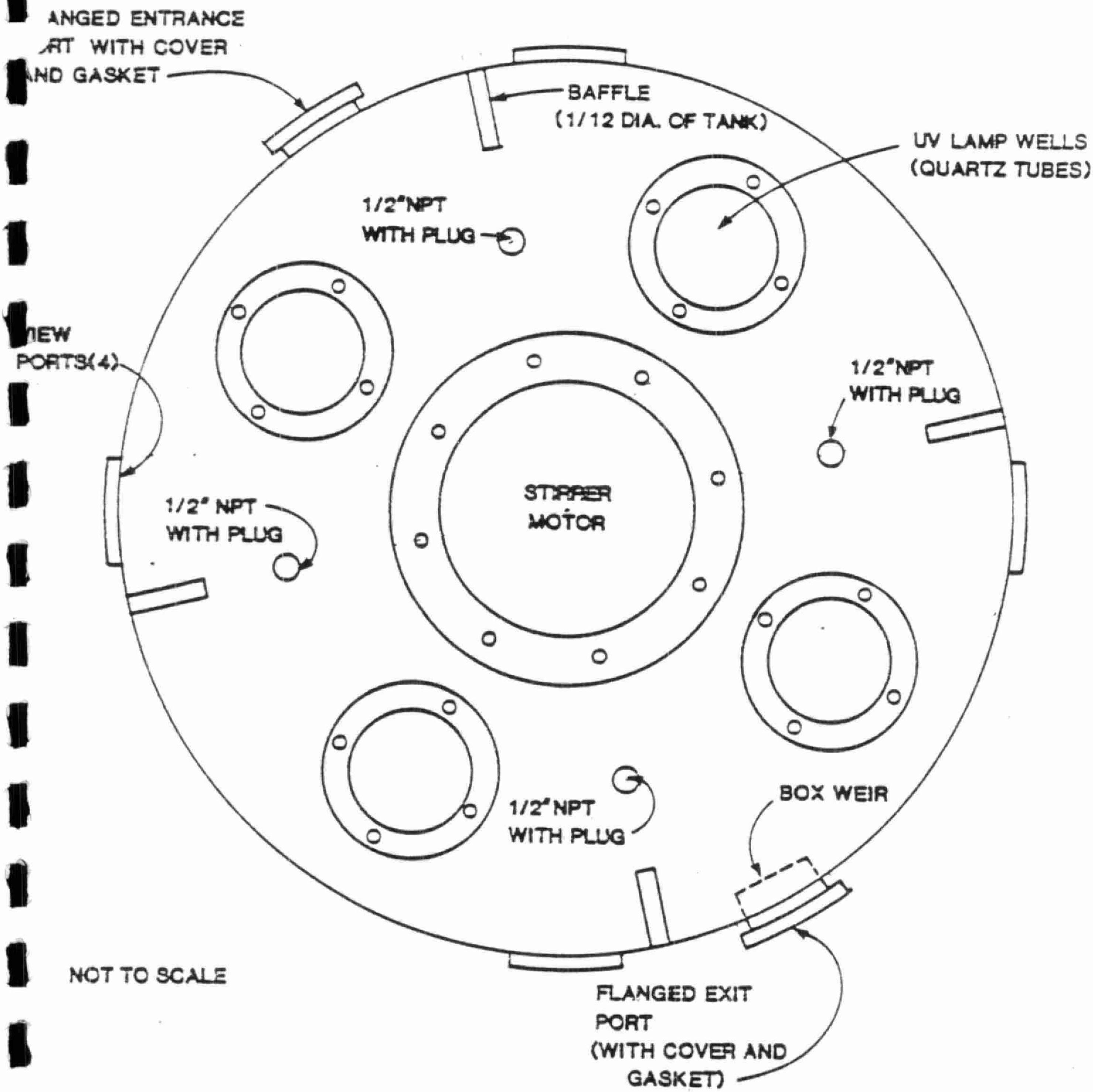
For comparative purposes, 99 per cent removal of TCE utilizing O_3 alone at 5.4 mg/L would require more than 90 min contact time.

Pilot studies are underway with O_3/H_2O_2 examining pretreatment to produce a matrix favorable to hydroxyl radical. Initial work with softening to lower bicarbonate ion, a hydroxyl scavenger, indicates TCE destruction significantly greater than that given in Figure A-1.



STIRRED TANK REACTOR

FIGURE 4A



CSTR (TOP VIEW)

FIGURE 4B

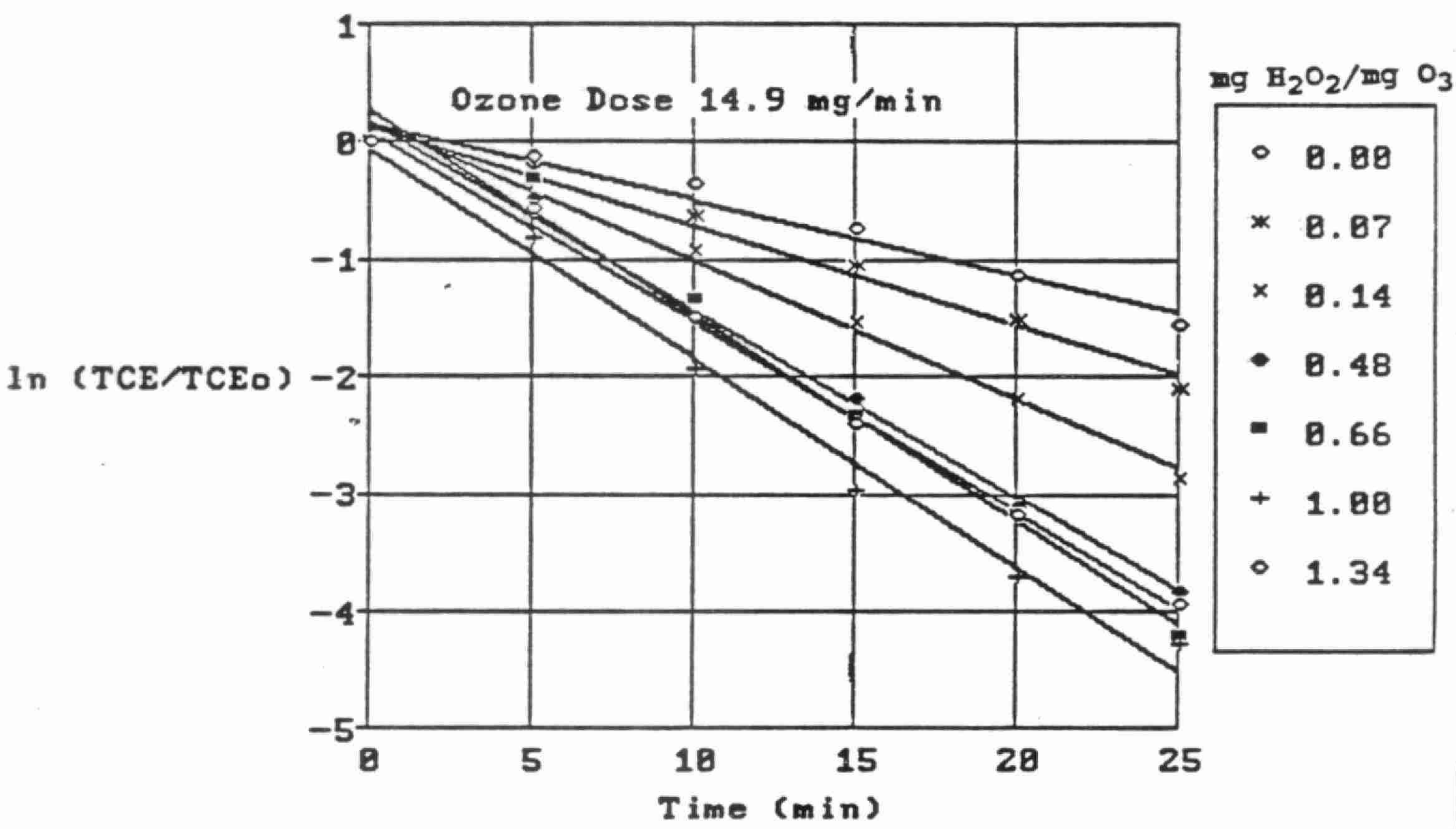


FIG. A-1 : RATE DATA FOR OXIDATION OF TCE WITH O_3/H_2O_2 SYSTEM (O_3 DOSE : 14.9 mg/min)

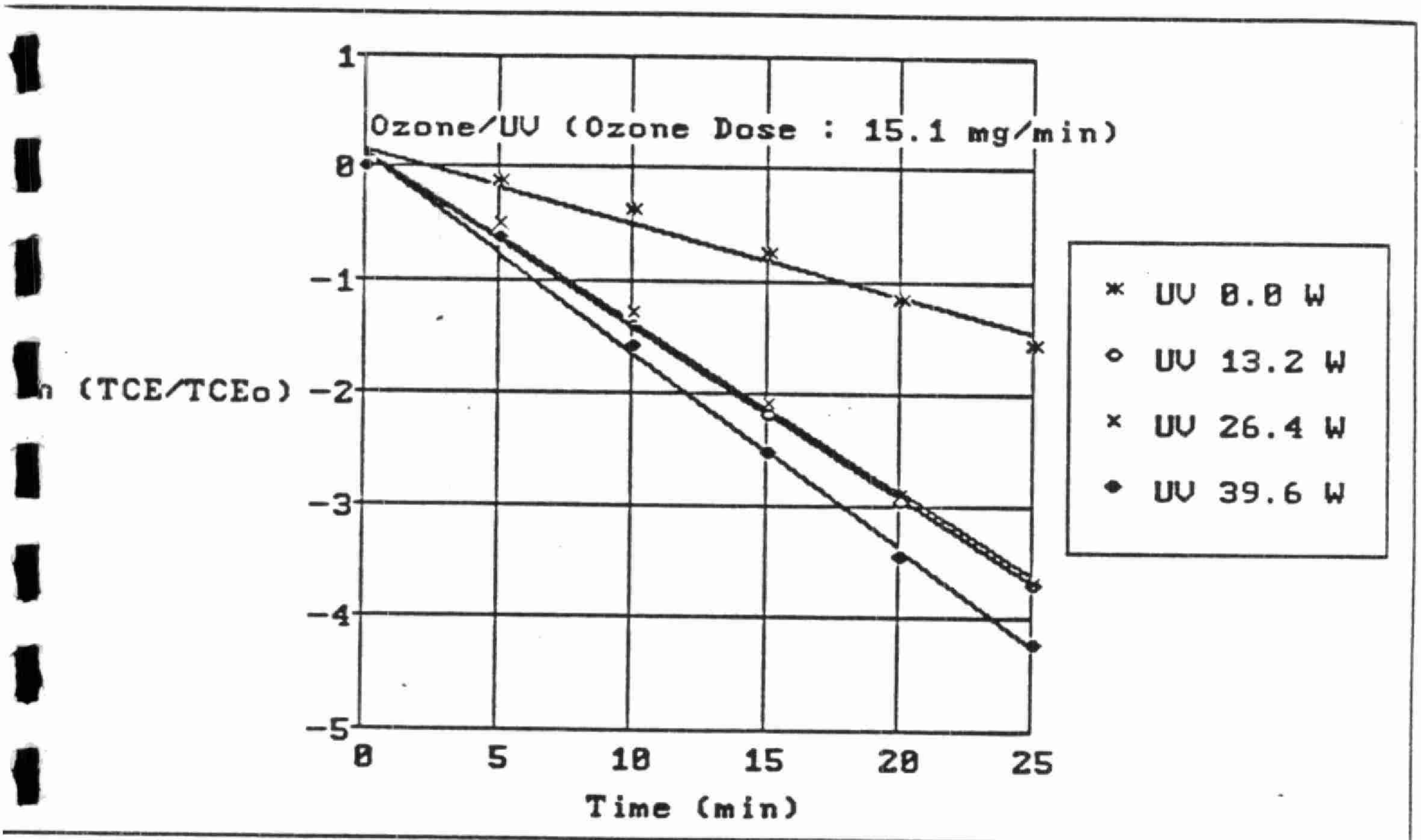


FIG. B-1 : RATE DATA FOR OXIDATION OF TCE WITH O_3/UV SYSTEM
(O_3 DOSE : 15.1 mg/min)

EMERGING WATER SUPPLY TECHNOLOGY AWWARF Code #: US-08

PROJECT DESCRIPTION

Project Title:

The Use of Membrane Technology for the Rejection of THM Precursors and SOCs

Contact (name of person, organization, address, telephone):

J.S. Taylor, Ph.D., P.E.
CEES Department
University of Central Florida
Orlando, FL 32816
(305) 275-2841

Project Description (Please attach a schematic diagram if appropriate):

Florida, as many other states, has high trihalomethane precursors in many potable water supplies most of which have relied on chloramination to control THMs to less than the MCL. This practice has resulted in a more colored than desirable finished water and THMs slightly less than the MCL. The projected decrease in the THM MCL will require many suppliers to seek new technologies for meeting the THM and color regulations. Additionally, the advent of SOC regulations in the amended drinking water regulations make some form of new technologies mandatory in the treatment of drinking water.

This project is primarily for the evaluation of membrane processes for the removal of organic contaminants. Color, TOC, THMFP, TOXFP, EDB, Chlordane, Alachlor, Methoxychlor, Heptachlor and Dibromochloropropane and the organic contaminants that have and will be evaluated to date. In addition the corresponding organic water quality is recorded. Any membrane processes is dependent on operating pressure and product recovery for cost of operating. The impact of product recovery and operating pressure on water quality and cost is being evaluated. Additional cost impact is controlled by the degree of pretreatment required prior to actual membrane. A primary objective of this project is to determine the degree of pretreatment required in order to utilize membrane processes for surface or ground waters that contain high concentrations of natural organics. Additionally, the change in finished water quality from membranes after use in such supplies is being evaluated. Finally, the required pore size or "tightness" of a membrane was evaluated for meeting the THM regulation.

Operating and cost data (including data on efficiency, results, etc.):

Operating data to date indicates that membranes processes can reject natural organic THM precursors more effectively than any other unit process utilized for water treatment. Pilot plant installations at the Village of Golf Acme Improvement District, Lee County and Flager Beach, all in Florida, have shown membrane with a molecular weight cutoff of 400 operating at pressures less than 150 psi and 75% recovery will reject 90+% of the THM precursors and 100% of the visible color. These membranes are referred to as nanofilters and are more similar to reverse osmosis membranes as opposed to ultrafilters. However, operating with a true RO membrane at pressure higher than 200 psi did not increase organic rejection but did increase inorganic rejection. Cost of a membrane plant is approximately \$0.50 to \$1.10/1000 gal for operation and \$0.70 to \$1.00/gal for capital cost.

Place(s) of installation/application (including dates):

Water Treatment Plants of:

Village of Golf, FL; September 1984-December 1984
Acme Improvement District, Loxahatchee, FL; January 1985-March 1985
Lee County, Fort Meyers, FL; February 1985-March 1985
Flagler Beach, FL; October 1986-October 1987

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

USEPA
WERL DWRD
26 West St. Clair St.
Cincinnati, OH 45268

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

EMERGING WATER SUPPLY TECHNOLOGY — AWWARF Code #: US-09

PROJECT DESCRIPTION

Project Title:

Use of Powdered Activated Carbon for Trace Organics Control

Contact (name of person, organization, address, telephone):

Vernon L. Snoeyink, Ph.D., Professor
Dept. of Civil Engineering
University of Illinois at Champaign-Urbana
208 North Romine
Urbana, IL 61801
(217) 333-4700

Project Description (Please attach a schematic diagram if appropriate):

This AWWARF sponsored project is being conducted by the University of Illinois at Champaign-Urbana, in cooperation with Lyonnaise des Eaux. The overall objective of the project is to improve the cost-effectiveness of powdered activated carbon (PAC) for trace organics control. The water quality problems for which PAC is best suited will be identified and promising ways of applying PAC to achieve contaminant removal will be identified. Specifically, the way PAC is currently used will be analyzed, including the removals that are achieved; the impact of water quality conditions and variability, plant design, and plant characteristics on the effectiveness of PAC; the cost of PAC application; and the best pre- and post-treatment to use in conjunction with PAC application. The effect of coagulants and polyelectrolytes on the kinetics of adsorption and equilibrium capacity of PAC, and the impact of these effects on the best point of PAC addition in a treatment plant will be determined. The efficiency of PAC adsorption of synthetic organic chemicals and total organic carbon in a laboratory floc blanket reactor will also be investigated (see attached schematic). A field test of the floc blanket reactor is planned at several water utilities.

The project began January 5, 1988 and will continue through May 1990.

Operating and cost data (including data on efficiency, results, etc.):

Place(s) of installation/application (including dates):

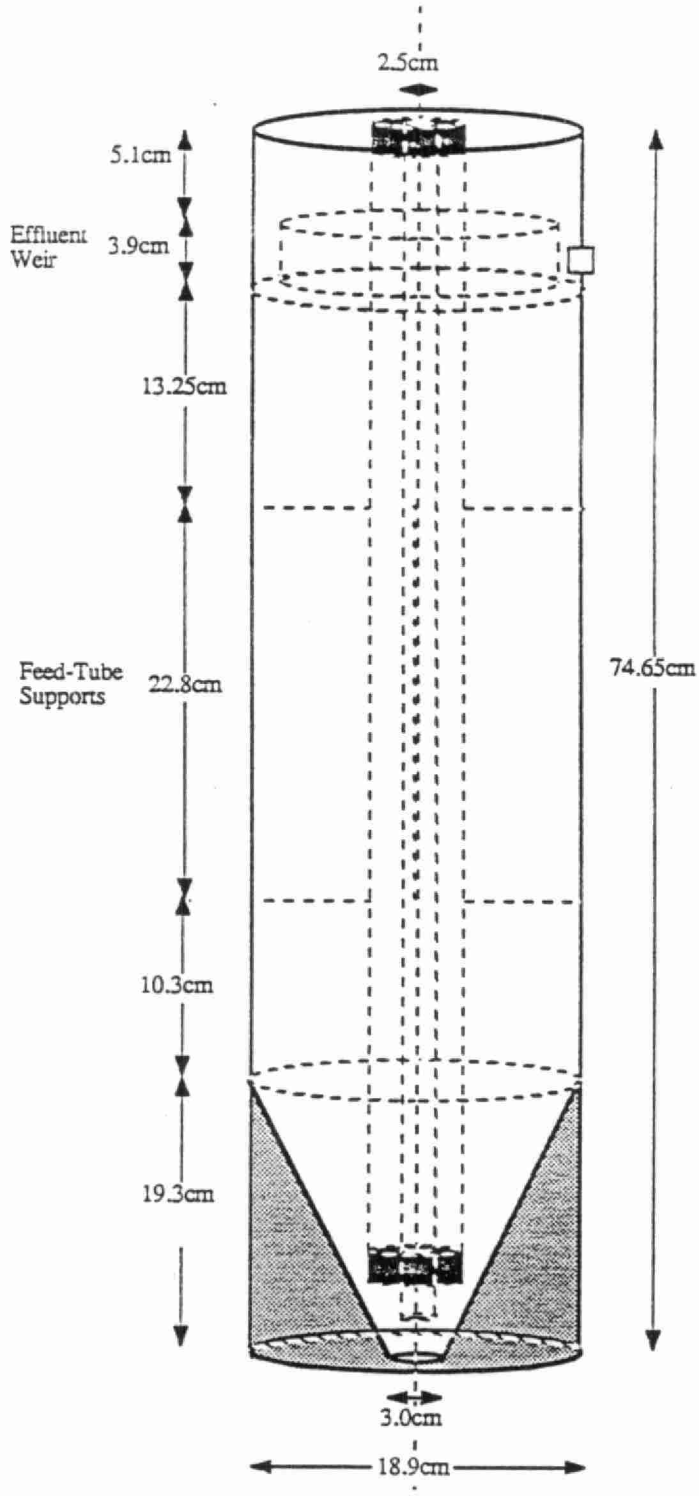
The floc blanket reactor will be field tested at two or more Illinois water utilities.

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

$100,000 AWWARF Funding
$ 84,000 Lyonnaise des Eaux funding

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.



Volume of Sections:

Feed Tube:	400 mL
Cone at Base:	1,370 mL
Main Body:	11,780 mL
Total Reactor:	13,500 mL

Figure 4.1: Floc Blanket Reactor

EMERGING WATER SUPPLY TECHNOLOGY

AWWARF Code #: US-10

PROJECT DESCRIPTION

Project Title:

Cascade Air Stripping System for Removal of Semi-Volatile Organic Contaminants

Contact (name of person, organization, address, telephone):

Dr. Richard E. Speece
Drexel University
Department of Civil Engineering
Philadelphia, PA 19104
(215) 895-2267

Project Description (Please attach a schematic diagram if appropriate):

This project will determine the practical viability of a novel counter-current packed tower cascade air stripping system (see attached schematic). Preliminary modeling results indicate the system may be economically and technically feasible for the efficient removal of semi- and low-volatile organic chemicals. The hydraulics, mass transfer, and pressure loss characteristics of the cascade air stripping system will be determined through pilot plant scale testing. The preliminary mathematic model will be refined and validated using the pilot plant results. Procedures for the design and scale-up of the cascade system will result from the study.

The project began September 1, 1987 and will end August 31, 1988. A final report on the project is expected to be available by late 1988.

Operating and cost data (including data on efficiency, results, etc.):

Place(s) of installation/application (including dates):

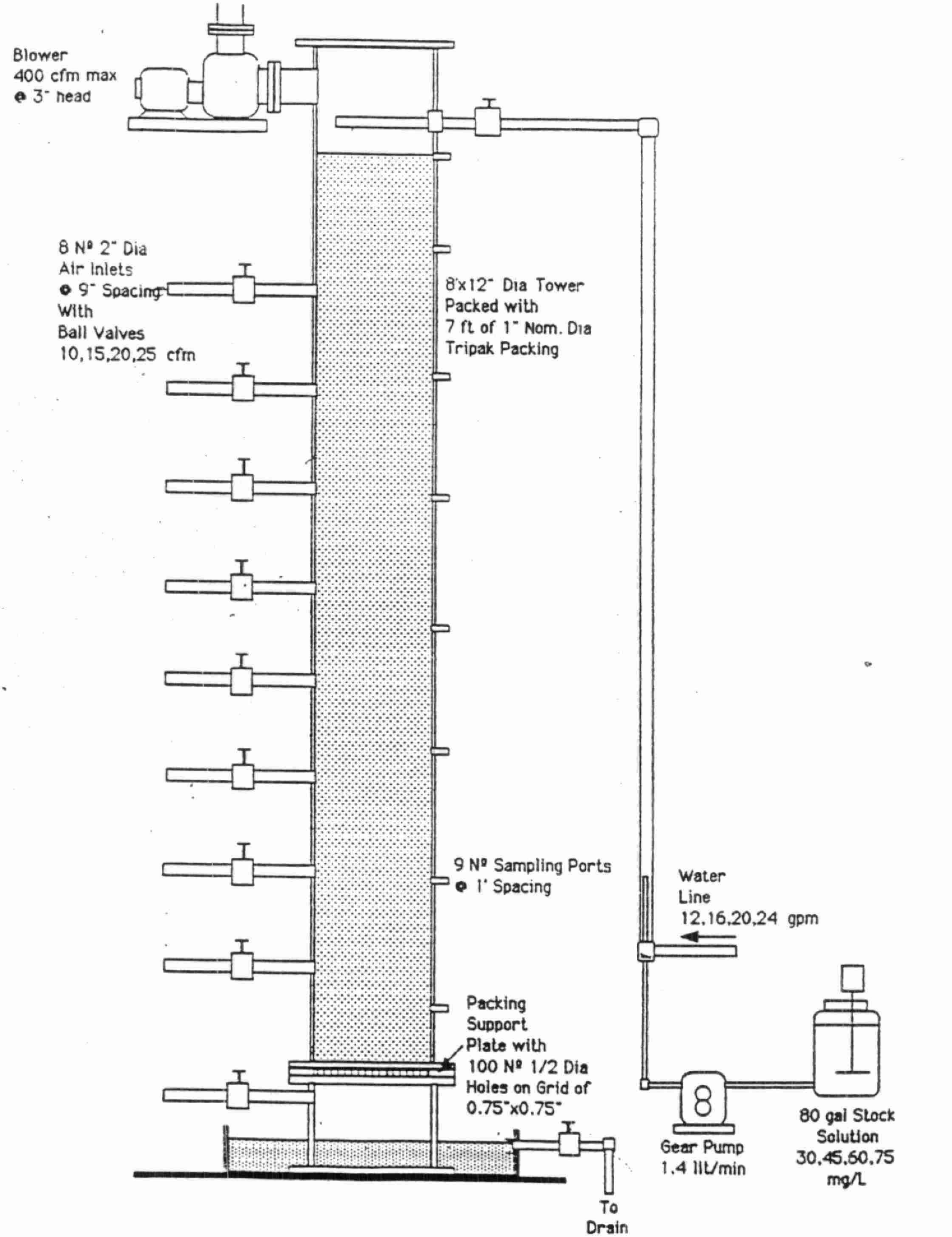
Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

$48,000 AWWARF funding
$12,000 Drexel funding

(Project #327)

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.


Blower
400 cfm max
@ 3" head
8 Nº 2" Dia
Air Inlets
@ 9" Spacing
With
Ball Valves
10,15,20,25 cfm
8'x12" Dia Tower
Packed with
7 ft of 1" Nom. Dia
Tripak Packing
9 Nº Sampling Ports
@ 1' Spacing
Water
Line
12,16,20,24 gpm
Packing
Support
Plate with
100 Nº 1/2 Dia
Holes on Grid of
0.75"x0.75"
Gear Pump
1.4 lit/min
80 gal Stock
Solution
30,45,60,75
mg/L
To
Drain

EMERGING WATER SUPPLY TECHNOLOGY AWWARF Code #: US-11

PROJECT DESCRIPTION

Project Title:

Evaluate and Modify Assimilable Organic Carbon Test

Contact (name of person, organization, address, telephone):

Don Reasoner (513) 569-7234
Gene Rice (513) 569-7204
Water Engineering Research Laboratory
USEPA
26 W. Martin Luther King Drive
Cincinnati, OH 45268

Project Description (Please attach a schematic diagram if appropriate):

Two projects are under way at EPA-Cincinnati related to measures of assimilable organic carbon (AOC). When lab techniques are working satisfactorily we will try to compare coliform growth in distribution systems to AOC of water entering the systems.

Operating and cost data (including data on efficiency, results, etc.):

None available.

Place(s) of installation/application (including dates):

Work underway at EPA-DWRD Laboratory in Cincinnati.

Patent staus, if applicable:

N/A

Other information (e.g., funding source, cooperating agencies, etc.):

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

EMERGING WATER SUPPLY TECHNOLOGY AWWARF Code #: US-12

PROJECT DESCRIPTION

Project Title:
Disinfectant Residual Measurement Methods

Contact (name of person, organization, address, telephone):
Gilbert Gordon Dept. of Chemistry Miami University Oxford, OH 45056 (513) 529-3336

Project Description (Please attach a schematic diagram if appropriate):

This project reviewed and summarized all disinfectant residual measurement techniques currently available for free chlorine (along with the various chloramines), combined chlorine, chlorite ion, chlorine dioxide, chlorate ion, and ozone. The final report includes not only the review of measurement techniques, but also guidance and recommendations as to what criteria water utilities should use in selecting residual monitoring techniques.

This project involved a comprehensive examination of literature on analytical methods used by analytical laboratories and water utilities worldwide, to elaborate on the various problems, advantages, disadvantages, and known interferences for each analytical method. The report describes the relative usefulness of each method along with know interferences (turbidity, organic matter, ionic materials, solids, color, buffering capacity) as well as the nature of the sample and the time between collection of the sample and the actual analysis. It was emphasized that almost invariably each of the methods described is based on the total oxidizing capacity of the solution being analyzed, and is readily subject to interferences from the presence of other potential oxidizing agents or intermediates from concomitant chemical reactions. Under ideal conditions some of the methods are accurate to better than $\pm$ one percent - especially in the absence of common interferences - whereas other methods are almost semi-quantitative with many common species interfering with both the precision and accuracy of the measurements.

The report describes in detail an "ideal" analytical method. Specific items included in this "Ideal Method" are accuracy, precision, reproducibility, lack of interferences, ease of use, and lack of false-positive values.

Operating and cost data (including data on efficiency, results, etc.):

The drinking water and wastewater industries can use the report to determine which analytical method(s) should be used to measure different oxidants. By selecting the most accurate and interference-free analytical method, the industry can confidently purchase or upgrade the required analytical equipment.

The report specifically identifies which methods are "recommended," "not recommended," or should be "abandoned" for both laboratory and field applications. The report is recommended as a companion document to Standard Methods for the Examination of Water and Wastewater.

Place(s) of installation/application (including dates):

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

This 816-page report is available in an abbreviated version entitled "A Survey of the Current Status of Residual Disinfectant Measurement Methods for All Chlorine Species and Ozone."

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

EMERGING WATER SUPPLY TECHNOLOGY AWWARF Code #: US-13

PROJECT DESCRIPTION

Project Title:

Disinfection of Bacterial Biofilms

Contact (name of person, organization, address, telephone):

Mark W. LeChevallier, Ph.D.
American Water Works Service Co.
1115 South Illinois Street
Belleville, IL. 62220
(618) 235-3600

Project Description (Please attach a schematic diagram if appropriate):

Experience has shown that maintenance of a free chlorine residual cannot be relied on to totally prevent coliform occurrences. Indicator bacteria have been isolated from drinking water containing as much as 12 mg/L free chlorine residual. This levels of resistance is thought to be due to attachment of bacteria to pipe surfaces. Clearly, disinfection theory of bacteria attached to pipe surfaces needs to be re-examined.

The current project was developed to examine disinfection of biofilm bacteria and to characterize the interaction of biocides with pipe surfaces. Disinfection of unattached bacteria yielded results similar to those found by other investigators. Unattached bacteria were quite susceptible to the variety of disinfectants tested. Viable bacterial counts were reduced 99 percent by exposure to 0.08 mg/L free chlorine residual (pH 7.0, 1-2°C) for one minute. For monochloramine, 94 mg/L was required to kill 99 percent of the bacteria within one minute.

Biofilm bacteria grown on the surfaces of granular activated carbon particles, metal coupons or glass microscope slides were 150 to more than 3,000 times more resistant to hypochlorous acid (free chlorine) than unattached cells. In contrast, resistance of biofilm bacteria to monochloramine disinfection ranged from 2 to 100 fold more than unattached cells. The results suggested that relative to disinfection of unattached bacteria, monochloramine was better able to penetrate and inactivate biofilm bacteria than free chlorine. For free chlorine, the data indicated that transport of chlorine into the biofilms was a major rate limiting factor.

Because transport was rate limiting, increasing the level of free chlorine did not increase disinfection efficiency. Experiments where equal weights of disinfectants were used indicated that the greater penetrating power of monochloramine compensated for its limited disinfection activity. These studies showed that monochloramine was as effective as free chlorine for disinfection of biofilm bacteria.

Experiments showed that attachment of bacteria to surfaces provided the greatest increase in disinfection resistance. Other mechanisms which increased disinfection resistance included: the age of the biofilm, bacterial encapsulation and previous growth conditions (e.g. growth medium, growth temperature). These factors increased chlorine resistance from two to ten fold. Importantly, the research showed that these mechanisms were multiplicative (e.g. that the resistance conferred by encapsulation could be multiplied by the resistance gained by attachment to surfaces). Given these results, it's easy to understand how bacteria can survive in chlorinated drinking water supplies.

Over the past several years, some utilities have reported some successes using unconventional biocides for control of coliform occurrences. Research conducted in this study showed that copper, zinc, sodium chlorite and alkaline pH has some effect on unattached bacteria, but little activity against biofilm bacteria. Some discussion is presented regarding concerns about applying heavy metals as bacterial biocides.

The research presented in this report report provide important insights into strategies to control biofilm bacteria. The research indicates that high levels of monochloramine may be effective for biofilm control. This approach could also produced secondary benefits such as: minimized taste and odor problems, lower trihalomethane (THM) formation, reduced pipeline corrosion, and less sloughing of debris from the pipe surface. Monochloramines will also provide a more stable disinfectant residual in dead-end lines.

Important research still remains to be completed to determine how to optimize disinfection of distribution system biofilms. While the current work suggest that certain properties of monochloramine allows it to better penetrate biofilms, experiments still not to be performed to determine the appropriate dose, pH, and the impact of temperature of disinfection. Considerations should also include the microbiology and the types of nutrients in the distribution system.

EMERGING WATER SUPPLY TECHNOLOGY AWWARF Code #: US-14

PROJECT DESCRIPTION

Project Title:

Predicting Water Quality in Distribution Systems

Contact (name of person, organization, address, telephone):

Robert M. Clark
Water Engineering Research Laboratory
USEPA
26 W. Martin Luther King Drive
Cincinnati, Ohio 45268
(513)569-7201

Project Description (Please attach a schematic diagram if appropriate):

EPA's Drinking Water Research Division has initiated a research project in conjunction with the North Penn Water Authority to develop and verify mathematical models for predicting water quality in a drinking water distribution system.

The first step in modeling the North Penn Water Authority water distribution system was to represent it as a link-node network using EPA's Water Supply Simulation Model (WSSM). In this representation of the system, the characteristics of tanks, pumps, valves and major water pipes are stored in WSSM and are available for modeling, display, reports, and analysis. Selection of major pipes for inclusion in the representation of the system is partially subjective but dependent upon pipe size, location of major demands and water quality sampling sites, and general importance of the pipe to the operation of the system. In all, the system is represented by 528 links and 456 nodes. Only the major connected network is included (i.e., North Penn's isolated satellite systems are not represented).

A hydraulic model used to simulate the physical behavior of the water distribution system was developed by the U.S. Army Corps of Engineers is referred to as the WADISO Model. For purposes of calibration and sensitivity analysis, both the steady state and dynamic options of the WADISO Model were used. Four water quality prediction models were developed. One is a steady state model based on a steady state hydraulic solution and the calculation of a mass balance at each node in the network. The second is a quasi-steady state model that attempts to simulate water quality changes for different time periods. The third is a contaminant propagation model that traces contaminants through the system and the fourth is a trace dynamic model based on a "marching out" solution. A continuous automated sampler is also under development.

Operating and cost data (including data on efficiency, results, etc.):

All four of the models have yielded excellent results when tested against available data. The steady state model was tested against routine monitoring data. An intensive 36 hour data collection study at six points in the distribution system was used to validate the quasi-steady state, contaminant propagation and dynamic models. All of the models predicted the propagation of trihalomethanes, chloroform, and hardness throughout the system. In addition to the modeling and verification, a continuous automated volatile organic chemical sampler has been developed using a patented EPA copying system and a commercial sampler. Partial documentation of the models is available upon request from the USEPA.

Place(s) of installation/application (including dates):

North Penn Water Authority, P.O. Box 591, Lansdale, PA 19446, USA

Drinking Water Research Division, WERL, USEPA, 26 W. Martin Luther King Drive, Cincinnati, OH 45268, USA

Patent staus, if applicable:

Not Applicable

Other information (e.g., funding source, cooperating agencies, etc.):

This project is being conducted in cooperation with the North Penn Water Authority. The Project Officer is Robert M. Clark of EPA's Drinking Water Research Division and the Principal Investigator is Judith A. Coyle of the North Penn Water Authority.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

Developing and Applying the Water Supply Simulation Model

Robert M. Clark and Richard M. Males

The Water Supply Simulation Model is a series of computer programs that allows for evaluation of the physical and economic characteristics of a water distribution system in a spatial framework. Development of the model and its application to the water supply system of the village of New Vienna, Ohio, are described.

Passage of the Safe Drinking Water Act has intensified interest in problems related to water supply and water utility management. Analysis of the regulations to be promulgated under the act indicates that some water utilities, particularly small ones, may be adversely affected economically.[1] An often-suggested option is that small systems combine with a larger system to form a regional water supply utility. It is assumed that the economies of scale associated with a regional water system would benefit the customers of small systems.

A characteristic of many production and transportation problems is the trade-off between the cost of building and operating facilities to meet demands for a product and the cost of transportation.[2] High transportation costs and low facility costs indicate decentralization; the reverse situation indicates a few large central facilities. These costs must be considered in planning, designing, constructing, and operating water supply systems.

It is possible to separate the water supply system physically into two components: (1) the acquisition and treatment function, and (2) the delivery (transmission and distribution) system.[3] Each of these components has a different cost function. The unit costs associated with treatment facilities are usually assumed to decrease as the quantity of service provided increases. The delivery system, however, is more directly affected by the characteristics of the area being served. The cost tradeoffs between the two components determine the cost of delivering water to any portion of the service area.

Because few analytical instruments are available for study of the economics of water supply systems, the US Environmental Protection Agency's Drinking Water Supply Research Division initiated a program to develop techniques and methodologies to evaluate the economics of regional systems. This article describes the development of a simulation model designed to aid in such an evaluation. The model can also provide insights into other water-related economic issues, such as spatial pricing and costing, conservation policies, operating improvements versus increased capital expenditure, user class subsidization, and fire protection capacity.

The model, called the Water Supply Simulation Model (WSSM), incorporates a series of submodels to describe the various economic, demographic, and hydraulic aspects of a water utility.

Model structure

The WSSM (Figure 1) is based on the concept of a water utility as a network providing service to a series of demands that are spatially distributed. The model can be used to analyze the costs of delivering water to these demand points. The service network is modeled as a link-node network, and it is assumed that water enters and leaves the system only at the nodes, which represent treatment plants, junctions, demand locations, and storage tanks. Water is carried between the nodes through connecting links (pipes). Costs are allocated to the various facilities and system components based on the amount of flow carried by that component.

The WSSM therefore requires that the water delivery and treatment system be described as a network of pipes, storage tanks, treatment plants, demands, and other hydraulic elements. Information concerning the network is stored in a network data base, including descriptive or calculated information about each element, such as size of pipe, geographic location of each demand, population associated with a demand, and connectivity of pipes (how one pipe is connected to another).

As a data base management system, the WSSM utilizes files that are permanently stored, as opposed to "decks" of data cards. The items of primary interest are the nodes and links of the distribution system. Two files are maintained—the node file, containing records for each node, and the link file, containing records for each link. The nodes and links define the network, and they are numbered as shown in Figure 2. The individual node and link numbers (identifiers or IDs) correspond to individual records in the link and node files. All records in a file are structured in the same general fashion (Figure 3).

The seven software modules used in the model are the establishment module, the editing module, the display module, the listing module, the hydraulic analysis module, the system solver module, and the input–output (I–O) module (Table 1). Establishing a data base for the WSSM requires the use of four of these modules.

TABLE 1
Major elements of WSSM

Element	Description
Network data base	Separate but cross-referenced data for the link and nodal elements of the network
	Standard and user-specified data items
Data base access methods	Routines designed for efficiency and ease of use Routines in standard FORTRAN, not strongly tied to a particular computer
Hydraulic network analysis model	Nonproprietary WATSIM model with both steady-state and dynamic simulation capabilities and ability to model a wide range of hydraulic elements
Other physical and economic models	Linear cost allocation procedure
	General purpose physical system solver to solve problems involving multiple sources, travel time, and mixing at nodes
Display and reporting modules	General purpose listing programs for link and nodal elements
	Flexible pen plotter display program for producing annotated maps of network
Data base establishment and edit modules	Establish comprehensive link and node files and check and cross-reference information in the two files, thus maintaining topological integrity of the network

The establishment module prepares a list of possible errors while creating the files, but no corrections to the input data are made. The display and listing modules are then used to verify the contents of the files, and necessary corrections are made with the editing module. Because of the importance of the integrity of the topologic and geographic information in the files, all modules except the key establishment and editing modules are designed to preclude destruction or distortion of these data.

The hydraulic module performs steady-state hydraulic network analysis, defining flow and pressure, given demands. The current version of WSSM uses WATSIM as the basis of the hydraulic module.[4]

The solver module is a general purpose algorithm that sets up and solves problems related to mixing in networks, given the network topology and flows. It is used with WSSM to solve three types of problems: (1) determining the travel time for any source to a node; (2) determining the concentration of any constituent at any node, given the concentration of the constituent at all sources; and (3) determining the cost of delivered water at any node, given the individual annual costs associated with the nodes and links of the system.

Both the solver and hydraulic analysis modules have the capacity to reinsert data into the data base, where they can be used for further calculation, listing, or graphical display.

The original concepts and approaches of the model were tested in a pilot study of the Cincinnati, Ohio, Water Works system. Figure 4 shows a contour map of various cost zones within the service area, which was developed from a pilot version of the WSSM. This approach allowed analysis and display of complex physical, policy, and economic situations and encouraged further development of the WSSM. A revised, more-general-purpose version of the model has been created, using the New Vienna, Ohio;[6] Kenton County, Ky.; and Tampa, Fla., water systems as "test-beds."

The New Vienna system

New Vienna is a village of approximately 1000 people (1980), located in Clinton County in the southwestern part of Ohio (Figure 5). The water supply system serves approximately 900 people and incorporates some 340 residential meters. Light industry, laundromats, and schools are also served by the system. The average metered use in the village is approximately 1.7 mil gal (6.4 ML) per month.

Water is supplied to the system from two sources: a well field and treatment plant, operated by the village, and purchased water from Highland County. Because the village is required to purchase a set amount of water each month from Highland County, it uses that water before switching over to its local sources. In a typical month, two thirds of the water is purchased.

The distribution system, which dates back to 1903, consists of pipes 8 in. (200 mm) and less in diameter, with the majority of pipes in the system being 4 in. (100 mm). A single elevated storage tank, with a capacity of 50 000 gal (189 270 L), provides load leveling and minimal fire protection. Plans are under development to provide additional storage. Operation of the system (Figure 6) is based on the water level in the elevated storage tank. Pumping starts at a pressure of 47 psig (324 kPa) and stops at 52 psig (358 kPa).

Elevations in New Vienna range from 1110 ft (338 m) to 1180 ft (360 m). The average total head for the system is approximately 1240 ft (378 m). Low pressures of about 23 psig (158 kPa) exist at the higher elevations during normal operations, but during fire fighting, pressures may drop to as low as 0 to 12 psig (0 to 82 kPa) in certain areas.

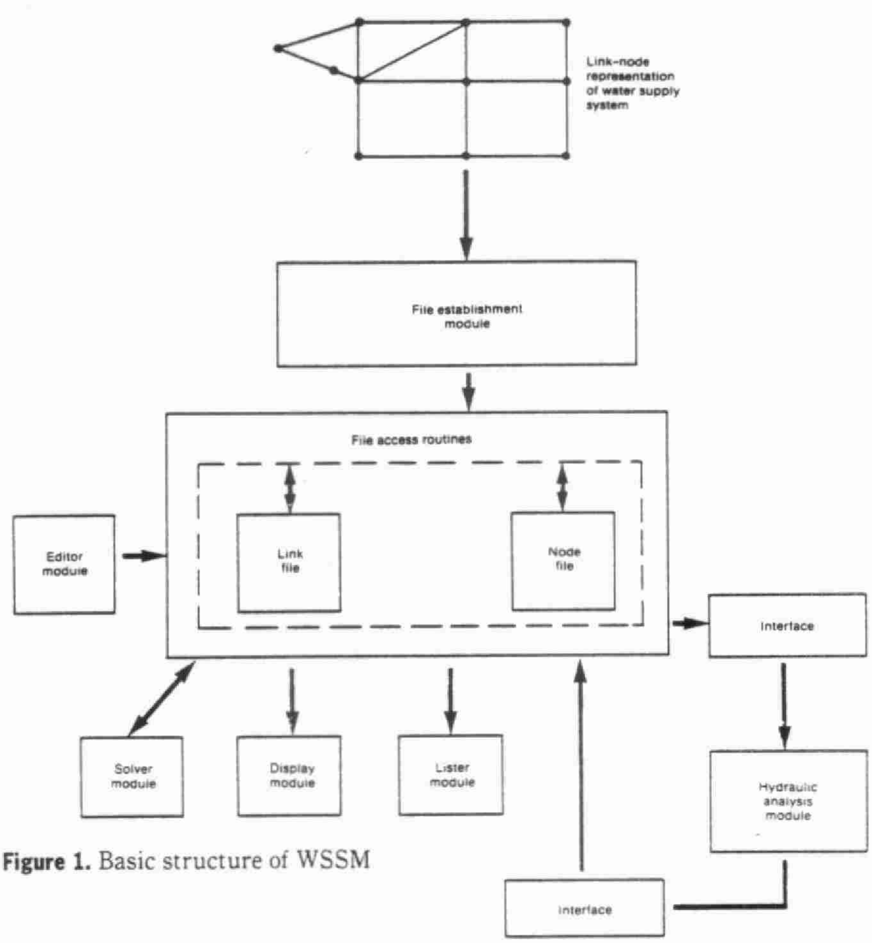


Figure 1. Basic structure of WSSM

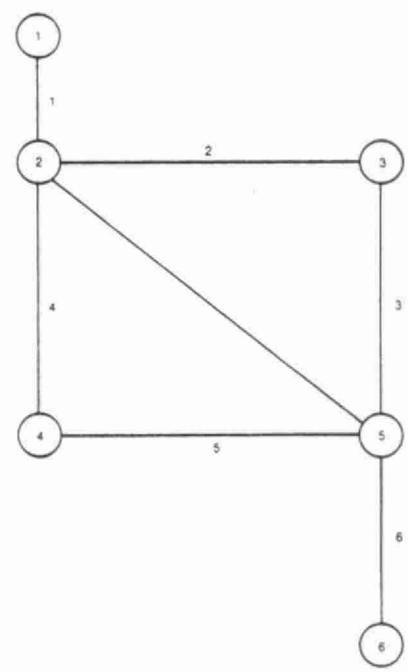


Figure 2. Node-link numbering scheme

Data base development

Development of the New Vienna data base consisted of the following steps:

- delineation of the distribution system in link-node form;
- determination of physical characteristics, for example, pipe size, and spatial coordinates;
- development of demand data; and
- development of cost data.

There is, of necessity, some interplay among these efforts to ensure that the link-node representation portrays the important changes in physical character of the system.

Delineation of system in link-node form. A link-node representation of the New Vienna water system was laid out on a gridded overlay to the base map (1 in. = 200 ft). Nodes were located in continuous lengths of pipe, based on their serving as centers of demand. Nodes were also located at pipe junctions and at changes in pipe diameter or type. To provide an accurate geometric as well as topographic map of the system, nodes were also located at major changes of pipe direction. Links and nodes were numbered sequentially. The New Vienna link-node representation consists of approximately 50 links and 50 nodes.

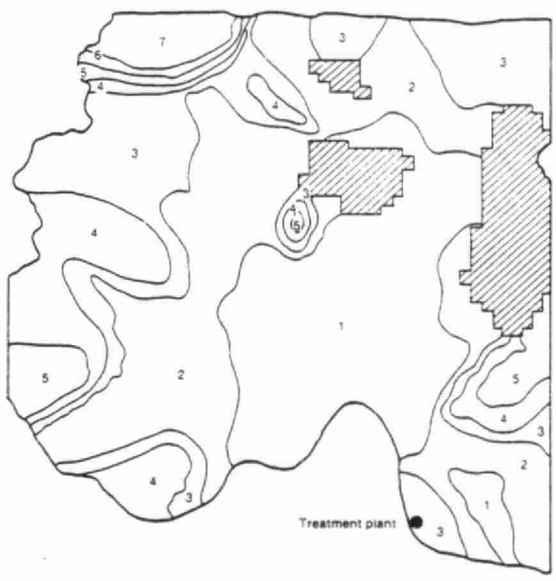
Determination of physical and spatial characteristics. Pipe lengths, types, and diameters were transferred from the base map to the link-node system and were associated with each individual link number. Topographic data, in the form of the "upstream" and "downstream" node numbers for each link, were also recorded from the base map. This information about the system sets the convention for flow throughout the WSSM, as well as providing topologic connectivity. By convention, flow in the pipe from the upstream node to the downstream node is positive, and flow into a node is positive.

The coordinate locations of each node were digitized through hand takeoff from the gridded overlay and were recorded. Elevations were obtained by placing the overlay on the base map and reading the elevation at each node from the contours. (Contours on the base map are at 3-ft [0.9-m] intervals.) Data for both the links and nodes were encoded and prepared as input to the file establishment module of WSSM.

Development of demand data. Although metered information is available for the majority of the customers, demand data were developed for other than industrial users by performing "house counts" within demand zones. Demand zones were drawn on the link-node overlay to arbitrarily relate demands to nodes. Each node has a demand zone, and it is assumed that any demands falling within that area are aggregated to the node.

Development of cost data. At its current state of development, the economic allo-

Figure 3. File and record structure



Zone	Cost $/1000 gal (3785 L)
1	0.15-0.20
2	0.20-0.29
3	0.29-0.38
4	0.38-0.47
5	0.47-0.57
6	0.57-0.66
7	0.66-0.76

Figure 4. Cost contours for Cincinnati Water Works service area, based on WSSM[5] *(1973 costs)*

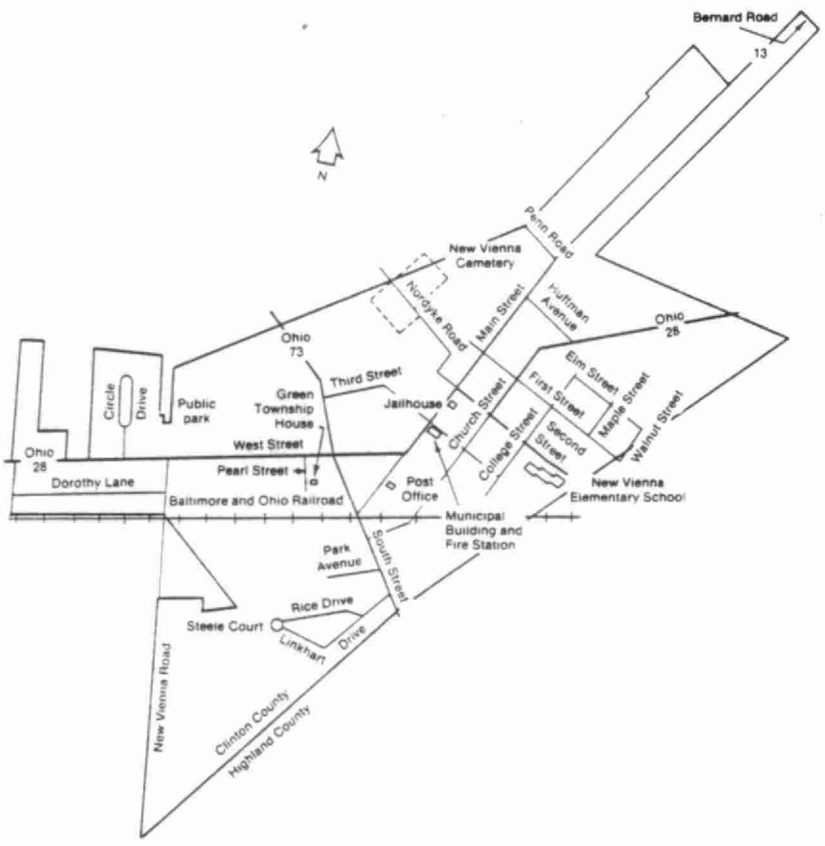


Figure 5. Map of New Vienna, Ohio

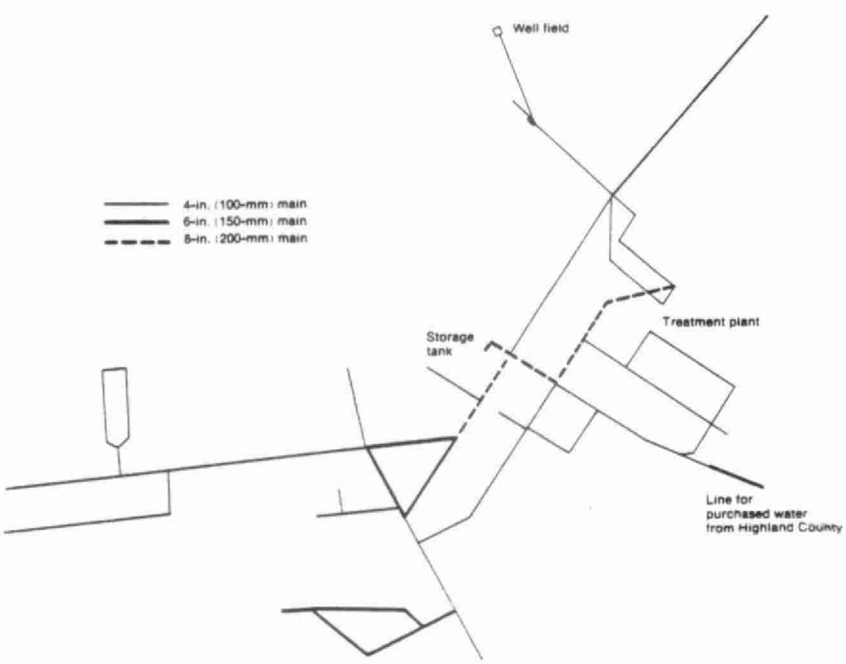


Figure 6. Schematic of New Vienna water supply system

cation procedure requires a single annualized cost, representing the combination of amortized capital and operation and maintenance (O & M) costs, for each node and link. For the case of New Vienna, actual construction costs were not available for most elements.[7] Capital costs, in general, were estimated as current (1981) replacement costs, which were then revised to actual year of installation through use of the three-digit *Engineering News Record* Construction Cost Index (CCI). Because the base year of the CCI is 1913, all system elements known to be installed prior to that date were treated as if they had been installed in 1913. Existing well and water treatment system costs were estimated based on cost curves derived from the publication "Estimating Water Treatment Costs."[7] Bid data for replacement of the elevated storage tank were used to estimate its cost. Pipe costs were based on unit prices in a construction bid for the area.

Annual O & M costs were taken from village records. Total O & M costs for 1981, including debt service and administrative costs, were projected to be $46 721. Cost summaries for the nodes and links showed the 1981 cost of construction, year of construction, CCI factor, original cost of construction (computed), and the 1981 O & M cost.

Use of WSSM for New Vienna

Once the basic description of the link-node network and its physical characteristics has been obtained, the data are encoded. These data are then used as input to the data base establishment programs, ESTBLINK and ESTBNODE. Program ERCHECK is run to test for topologic errors. At this point, it is frequently desirable to visually inspect the data base and to refer back directly to the base map. Accordingly, program NETPLOT is utilized to obtain a computer plot of the network at the desired scale. Program REPORTER also lists the data base, showing what information has actually been stored for each pipe and node.

Once the data base has been inspected and corrected, the hydraulic analysis module is used to determine pressures and flows for a given set of demands. The results are stored in the data base. Program NETPLOT is used to display these results (Figure 7), greatly simplifying the calibration process. Once an adequate hydraulic simulation is achieved, the solver module is used to determine costs, travel time, and nodal concentrations. Figure 8 is a computer-generated contour plot showing the unit costs of delivered water at the nodes of the New Vienna system.

It should be noted that WSSM does not provide answers, but rather is a tool for managing and displaying water

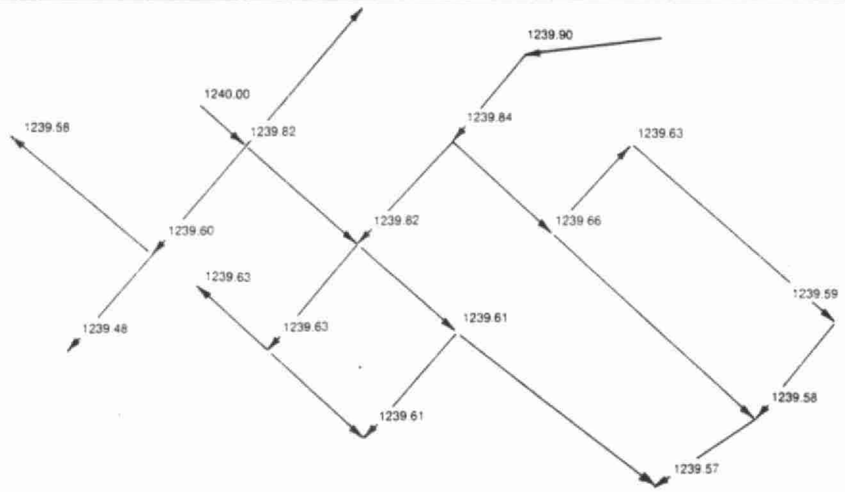


Figure 7. NETPLOT display of head at nodes (in feet) and flow direction

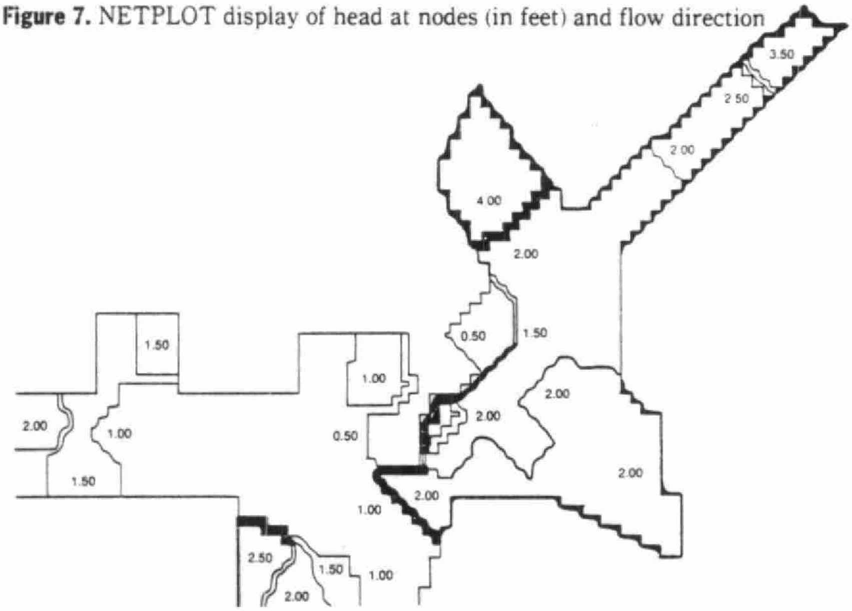


Figure 8. Cost contours ($/1000 gal [3785 L]) for New Vienna

supply network data. The WSSM technology is designed to aid the researcher, engineer, economist, and planner.

Summary and conclusion

The Water Supply Simulation Model can be used to provide spatial cost allocation, time of travel, and contaminant concentration information for a water supply network. Development of this model allows additional insight into the treatment and delivery of water. The approach employed in the WSSM is general in nature and is not restricted to water supply problems. In fact, the model should be applicable to the analysis of any service delivery system that can be characterized as a distribution network overlaid on some spatial distribution of supply and demand.

Some potential future studies of the WSSM include:

- exploration of the impact of design for fire protection and of the manner in which beneficiaries of this nonconsumptive use of water are assessed;
- further exploration of peak and off-peak considerations, and simulation of pricing strategies;
- use of the concentration and time-of-travel capabilities of the WSSM to simulate quality differences in multiple-source systems and to study the transport and decay of waterborne pollutants through the system;
- further examination of spatial methodologies for parameterizing hydraulic network analysis models in a simple manner;
- use of the graphic capabilities of the WSSM in other arenas, such as pipe break and water quality data; and
- examination of the effect of the water supply network on land development patterns and of the interrelationship between the water supply network and the waste collection network.

Acknowledgment

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DISTRIBUTION SYSTEM SYMPOSIUM PROCEEDINGS: Presented at the AWWA Distribution Division Symposium, September 7-10, 1986, Minneapolis, Minnesota

PREDICTING WATER QUALITY IN DISTRIBUTION SYSTEMS

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INTRODUCTION

The quality of a public water supply although acceptable when it leaves the treatment plant, may deteriorate before it reaches the user. Deterioration may be caused by either chemical or biological transformations or by a loss of system integrity. There have been a growing number of coliform regrowth and biofilm formation situations reported in distribution systems.

Mechanisms that may cause this deterioration include chemical and biological transformations, or loss of system integrity. Organics and other nutrients may enter into the water distribution network with the raw water, may be produced during treatment or enter through leaks, or cross connections. Growth or regrowth may be observed in distribution systems despite treatment and disinfection at the treatment plant which is intended to eliminate such microbial activity.[1] Microbiological growth may occur in the network, in the water or on the walls in the form of biofilms. Bio-cells may be trapped in mineral deposits known as tubercles. Growth occurs at the expense of the nutrients in the water and if disinfectant residuals cannot be maintained throughout the entire distribution system the potential for growth in pipe networks is greatly enhanced.

In addition to the microbiological degradation that may take place in the water in distribution systems there is the problem of chemical deterioration as well. For example, corrosion byproducts may occur when material is leached from the walls of pipes. High concentrations of lead may occur in household plumbing systems if aggressive water is distributed to the customer. Figure 1 illustrates some of these deterioration mechanisms. Figure 2 is a more detailed illustration of the interactions that take place at the pipe wall interface.

Table 1 contains a list of municipalities that reported coliform regrowth situations in the United States. Table 1 illustrates the concern over maintenance of water quality in distribution systems as delivered to the customer.[2] In response to this concern EPA's Drinking Water Research Division has sponsored a series of projects that deal with distribution system problems. This paper will briefly review EPA's

distribution system research. Research into the development of models for predicting water quality variations in systems will be discussed in some detail.

A water quality prediction model has been developed in cooperation with the North Penn Water Authority. This cooperative agreement has focused on the hydraulic behavior of the system, examination of historical water quality sampling data, and steady-state modeling of water quality within the distribution system. The steady-state model has been developed and field tested. A dynamic model is under development. The results of this work suggest that the dynamic features, of system behavior, such as variations in water quality, changes in demand and mixing of water from different sources, will be significant in predicting water quality in distribution system.

EPA's DISTRIBUTION SYSTEM RESEARCH

EPA's research in distribution system problems may be classified into three major categories: microbiological studies; corrosion studies; and, infrastructure/system studies. Microbiological studies have focused on developing new techniques for recovering and identifying organisms. Research is being conducted into: development of the concept of assimilable organic carbon; examination of stressed organisms; understanding the mechanisms and causes of biofilm formation; identifying and classifying tubercles; and, investigating and understanding problems related to coliform regrowth studies. Studies have been conducted to determine the extent of lead leaching from household plumbing and into factors effecting deterioration of asbestos cement pipe. Work has also been conducted on development of corrosion indicators and chemical corrosion kinetics. In the infrastructure/system area, a microcomputer system for maintaining break and leak complaints records has been developed.[3,4] Statistical measures for assessing the probability of breaks and leaks occurring in networks are being developed and attempts are being made to determine the physical factors causing breaks and leaks. Research is being conducted to acquire an understanding of the hydraulic conditions that affect biofilm formation. Techniques for predicting water quality in distribution systems are being developed.

MODELING RESEARCH

Distribution system modeling is very complex. Variations in system flow occur because of the way in which the system has been designed. Hydraulic analysis and verification of flows in a system is an art in itself. Predicting demand is also an art. Demand variations complicate the problem of predicting and modeling flows in distribution systems. Hydraulic and demand variations, the mixing of water from different sources, and the kinetics of formation of biological and chemical products all make the modeling of water quality in distribution systems a complex and difficult process. Two approaches to predicting water quality in distribution systems are described in this paper. One approach is based on a steady state modeling concept and has been verified by field evaluation.[5] The other is a dynamic modeling approach for which an algorithm has been developed and which will be described in this paper. The North Penn Water Authority north of Philadelphia, PA. was used as a test case for this research.

THE NORTH PENN SYSTEM

The North Penn Water Authority has an average production of 5 million gallons a day, and consists of ten municipalities with 225 miles of pipe. It serves over 14,500 customers and has three pressure zones plus several small satellite systems. Its water sources include purchased treated water which amounts to about one million gallons per day of supply plus 40 individual wells. There is wide variation in water quality from these different sources. Figure 3 shows a schematic of the North Penn Water Authority distribution system. The Keystone tie-in is the surface water source coming into North Penn from the south. The various wells in the Lansdale low pressure zone, Lansdale high pressure zone and Souderton high pressure zones are shown. Pressure zone boundaries are shown as dotted lines and storage tanks are shown by inverted triangles. Compliance or routine sampling points used for monitoring are designated by "x".

In order to perform the hydraulic analysis a link and node representation of the network was used. Beginnings of pipes, junction of pipes as well as tanks are represented as nodes and the pipes themselves are represented as links. Hydraulic models were used to determine flows in the links.[6,7] In the steady state analysis it is assumed that consumer demands and tank flows and heads are constant. The resulting steady state or equilibrium flows and velocities throughout the system are then determined. In dynamic or quasidynamic modeling, demands, inflows, and tank heads, are fixed for a time period and the steady state solution calculated. During the next period, tank conditions are calculated based on flows and tank elevation in the previous period. New demands and inflow conditions in the next period are used to determine a new steady state solution. In the true dynamic solution, there is transient behavior in the system. The water in the system travels in a wave at a speed much greater than the actual flow, but for all practical applications the quasi-dynamic solution is acceptable.

STEADY STATE SOLUTION

In order to determine and predict the steady state concentrations of contaminants in the distribution system, a steady state hydraulic solution was used along with the known concentrations in the water sources to determine the resulting steady state spatial distribution of concentrations throughout the network. The approach used was to formulate a mass balance around each node and solve for the resulting concentrations.[8,9] The development of the equations at a node is illustrated for the specific case shown in Fig. 4, in which two pipes deliver water to node i, and there is a single discharge link delivering water to node x.

The flow directions and quantities are known because it is assumed that the network has previously been solved hydraulically. We can define Q_{ij} as the flow into node i from node j. Q_{ij} is thus equal to $-Q_{ji}$. We consider the unknown concentrations of the constituent of interest at nodes i, j and k, to be C_i, C_j and C_k, respectively. The known volume of flow from an external source delivering water to node i is S_i, and the known constituent concentration in the external source is SC_i. For the sake of simplification of notation, the total influent water from all sources to node i is defined as I_i, and in the case shown in Fig. 4, this quantity = $S_i + Q_{ik} + Q_{ij}$.

By mass balance for flow at node i, the flow leaving node i for node x, Q_{xi}, is given as follows:

$$Q_{xi} = S_i + Q_{ij} \tag{1}$$

By mass balance for the constituent itself, assuming complete mixing at node i:

$$C_i = \frac{[(Q_{ik}*C_k) + (Q_{ij}*C_j) + (S_i*SC_i)]}{I_i} \tag{2}$$

Eq. 2 states that the average concentration at node i of the constituent of interest is equal to the total mass of the constituent delivered per unit time from all influent sources to node i, divided by the total quantity of influent flow at node i. By definition then, the concentration in link xi = C_i.

For the complete network, the flows and flow directions are known by a previous solution of the hydraulic network, and all Q_{ab} and I_a are known for all nodes a and b. Assuming n nodes in the network, we have n equations of the general form of Eq. 2 (with one C*Q product contributed for each link influent to the node), and n unknowns, the C_i at each of the n nodes. The external source quantities and concentrations are known as boundary conditions for each of the nodes at which water enters the network from an external source. The equations are linear in the unknown concentrations, and can readily be solved by standard methods. As with the case of the hydraulic analysis of networks, the coefficient matrix thus developed is sparse, and can profitably take advantage of sparse-matrix simultaneous equation solution techniques.

This concept has been discussed elsewhere and is called the SOLVER algorithm. In the steady state solution the SOLVER algorithm was applied to the main pressure zone of the system which represents 75 percent of the system demand. A hydraulic scenario considered to be representative of "average" conditions was selected. Wells are assumed to be on and water is flowing into the evaluated Chestnut Street and Lawn Avenue tanks. Model predictions were made of concentrations associated with Keystone water throughout the Lansdale low pressure zone. Trihalomethane concentrations were used as a tracer in the system because of the surface water from the Keystone tie-in.[5] There are no triahalomethanes formed in the groundwater, and it was assumed that the triahalomethanes from surface water represented a relatively steady state concentration having exhausted the triahalomethane formation potential. The SOLVER algorithim was applied to North Penn for average TTHMs (47 micrograms per liter).

Figure 5 represents information gathered from routine TTHM surveillance information at North Penn for the date 4/16/84. Figure 6 represents the TTHM data for 4/16/85 and Figure 7 represents the average TTHMs concentration using surveillance data collected over a two year period. One can see the rather gradual decline from 45 micrograms per liter at Keystone to below 10 or 20 in the eastern, western and northern parts of the system. Figure 8 represents the steady state modeling predictions for the THMs. An examination of Figure 8 (as compared to Figure 7) shows that under steady-state conditions the model under-predicts the observed TTHM values to the north and west (near Lawn Avenue and

Harleysville respectively), but provides a more reasonable estimate of observed values in the central, eastern, and southern areas of the Lawnsdale pressure zone. However steady state solutions are unrealsitic and limiting, therefore, a dynamic algorithm for predicting water quality has been developed.

DYNAMIC MODELING

Under dynamic conditions system demands and supplies are variable and there are temporal and spatial variations in quality. In order to investigate the nature of water quality variability within the system, an intensive sampling system program was conducted at six sites. Figure 9 shows the various sampling points used in the field study and Figure 10 depicts the results of the intensive sampling program using total trihalomethanes (TTHMs) as a tracer. One can see that there is quite a bit of variation at a given point within the 30 hour period, and that there is also quite a bit of variation within the system itself. Hardness is representative of the well water and is shown in Figure 11. At the Mainland sampling point a flushing back and forth of water between the surface source to the well source can be seen. The peaks of the TTHMs at Mainland are approximately 6 hours out of phase with the peaks from the wells indicating that water flow at this point is affected by the surface and ground water sources.

This analysis points out the problems in attempting to predict a dynamic situation using a steady-state mode. The average TTHM data represent long-term averages, of data taken over a number of years, at different times of the day. The pattern of flow in the NPWA distribution system varies during the course of a day, as wells cycle off and on. Late at night, when most wells are off, Keystone water is the primary source of supply for the Lansdale low pressure zone system, and this water passes into the western and northern portions of the system, where it can enter the Lawn Avenue tank. During times of the day when Lawn Avenue tank water enters the Lansdale low system, this water can be expected to have non-zero TTHM (due to the origin of at least a portion of this water from Keystone when Lawn Avenue is filling). The pilot sampling run of November 14-15, 1985 shows a range during the sample period from a maximum TTHM value of 36 ug/L to a minimum of 13 ug/L, at the inlet to Lawn Avenue. This range is consistent with the historical data of Figure 7, where a value of 18.8 ug/L is shown in the neighborhood of Lawn Avenue. Examination of the daily THM historical data of Figures 5 and 6 also shows elevation of TTHM towards Lawn Avenue, and higher values in the Souderton pressure zone, in the region of 12-16 ug/L, presumably from Lawn Avenue water pumped into the Souderton zone. Data from the pilot sampling run, taken at the Mainland sampling site, shown on Figure 10, shows TTHM values in the range from 9 to 34 ug/L, with significant variation. As concluded by the analysis of the pilot sampling run, Mainland has water from the wells in Harleysville (NP14, NP31, NP11, NP20, NP26, NP48) during the times of day when they are pumping, and from Keystone in the early morning hours. Historical data shows levels of TTHM of 2 to 6 ug/L in this area, as compared to the model prediction (with wells on) of 0 ug/L. The model does show, however, that the zone of blending of Keystone and well water is fairly close to Mainland, and thus, simply from an examination of the model prediction, Mainland would be expected to show the variations that it in fact does show. (The Mainland site was selected primarily to test this hypothesis in the pilot sampling run).

While the initial steady-state modeling did provide useful information, in particular insofar as design of the pilot sampling study was concerned, it was obvious that the attempt to model the dynamic nature of the complex NPWA system with a single steady-state predictive model run, proved inadeuqate. Accordingly, an attempt was made to extend the steady-state predictive principles to "quasi-steady-state" modeling for the situtations encountered in the pilot sampling run. The development of this dynamic algorithm is described in the next section.

DYNAMIC ALGORITHM DEVELOPMENT

In this approach velocities for a given time period were calculated and a time step determined within the fixed period. Decay coefficient are incorporated for modeling non-conservative contaminants. Initial conditions for the system were determined by interpolating concentration at the nodes. After the system is "started" concentrations at a node for a given time step are calculated as the flow weighted concentration of all flows entering the node. Figure 12 shows the general routing procedure that is used for time steps within a given period and the equivalent distance that a contaminant wave front moves down the pipe. The horizontal axis shows the movement of a packet of water forward in time and the vertical axis shows the packet of water as it moves down the pipe. When the wave front intersects a given node it is reflected in the concentration at that node.

Figures 13 through 15 illustrate the application of the dynamic algorithm to a small hypothetical system shows with various initial contaminant concentrations at each node. For example, at node A, the initial concentration of a contaminant is given as 100. Figure 14 depicts the hydraulic system after the system has solved for the conditions that hold in period 1. Figure 15 illustrates the way the flow varies in the pipe with the time steps within period 1. The upper left corner is Period 1 at time step zero. Moving through the various time steps in a period allows one to see the routing of a given packet of water in the pipe. Time step 16 represents the last time step in period 1.

Figure 16 shows the flows and demands that exist in the pipe network during period two under a given set of demand conditions. Figure 17 shows the contaminant movement in Period 2. Figure 18 is intended to summarize the variations in quality that take place spatially in the system. The contour plots show the movement of the contaminants in the network over a period of time. This analysis illustrates the enormous amount of variability that can take place within a distribution system based on time, hydraulic demand and other time varying conditions.

SUMMARY AND CONCLUSIONS

There are many possibilities for water quality deterioration in drinking water distribution systems. There is growing concern over the occurrence of coliform regrowth incidents and water borne disease outbreaks in the U.S. The Drinking Water Research Division of EPA has invested considerable research in examining various types of distribution system problems. These include microbiology, corrosion and infrastructure/system studies. One major area of investigation is the examination of variation of water quality and the effect of mixing in distribution systems and the ability to predict these variations. DWRD has initiated a cooperative agreement with the North Penn Water

Authority to study these variations in system water quality. Data from this study has verified the steady state modeling efforts. However, more effort is needed to establish the ability to predict dynamic variations in water quality.

Results of a short-term sampling run clearly show that significant differences in measured quality can be obtained in a multi-source distribution system, depending upon the time and location of sampling. This may have major implications for compliance monitoring strategies.

Initial steady-state modeling predicted that variations in water source and flow reversals would likely be seen at the Mainland sampling location. This pattern was in fact found. A more detailed analysis of the predictive capacity of steady-state modeling can at least predict zones in which such variations may be found.

The variation in TTHM at Keystone suggests that operational parameters are influencing the quality of the finished water. This variation was greater than expected, as it was assumed that the Keystone water would be relatively constant in quality over the period of the sampling run. Additional studies of Keystone water, using a shorter sampling interval and longer time spans, so that more diurnal cycles could be examined, will be made.

To date, it appears that most examination of dynamics of water in distribution systems has been restricted to hydraulics, with the general assumption that the quality of the product has been more or less constant. Perhaps the major conclusion that can be drawn from this effort is that examination of quality in water distribution systems must take into account spatial and temporal variations, and that assumptions relative to long and short-term constancy of behavior do not appear to be borne out. Ultimately these models will be very useful in designing future water quality surveys.

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TABLE 1. COLIFORM REGROWTH SITUATIONS INVESTIGATED BY U.S. EPA

Community	Popultion Estimate	Year
Muncie, IN	77,000	1980
Seymour, IN	15,000	1980
Bethlehem, PA	70,000	1981
Wilmette, IL	28,000	1981
Terre Haute, IN	61,000	1982
Springfield, IL	100,000	1982
Lexington, KY	204,000	1982
Florissant, MO	55,000	1984
Kennebunk, ME	3,000	1984
New Haven, CN	760,000	1984-1985
Minneapolis, Fairground, MN	250,000	1985
Monmouth, NJ	100,000	1985
Louisville, KY	298,000	1985
Iowa City, IO	50,000	1985
Fort Thomas, KY	16,000	1985

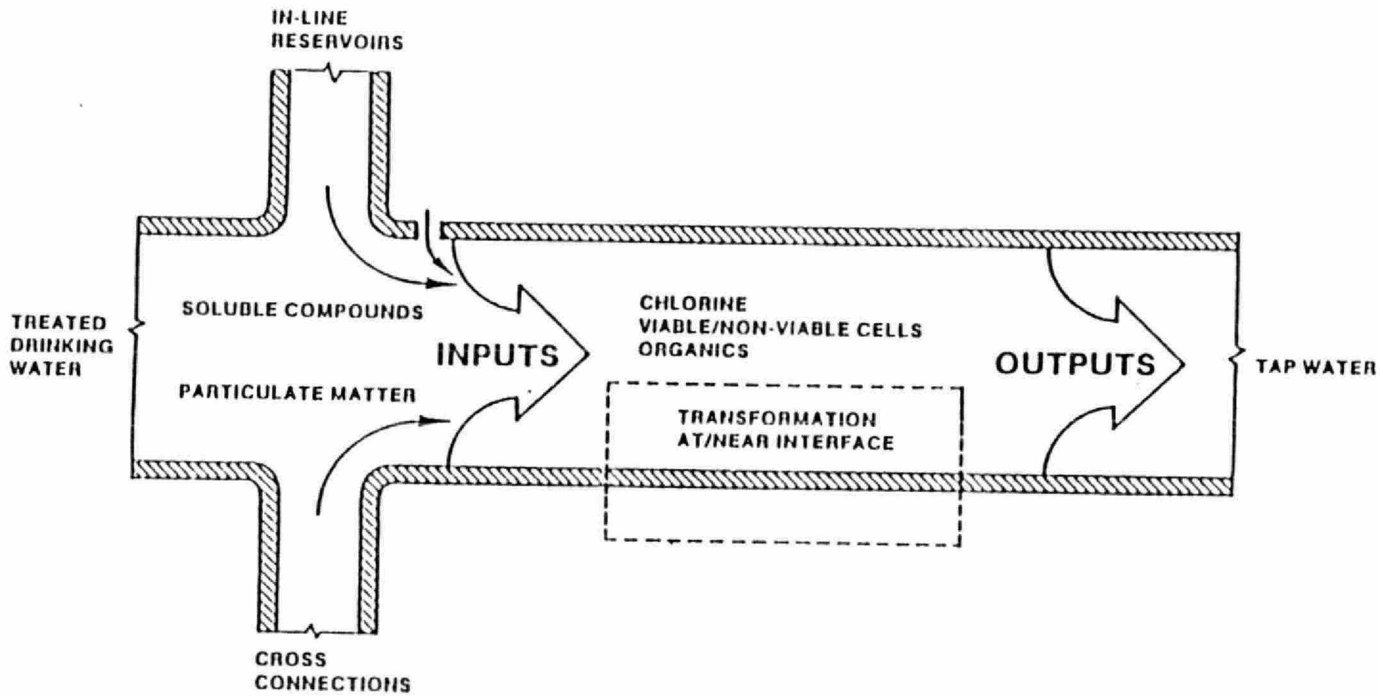


FIGURE 1. WATER DISTRIBUTION PIPE

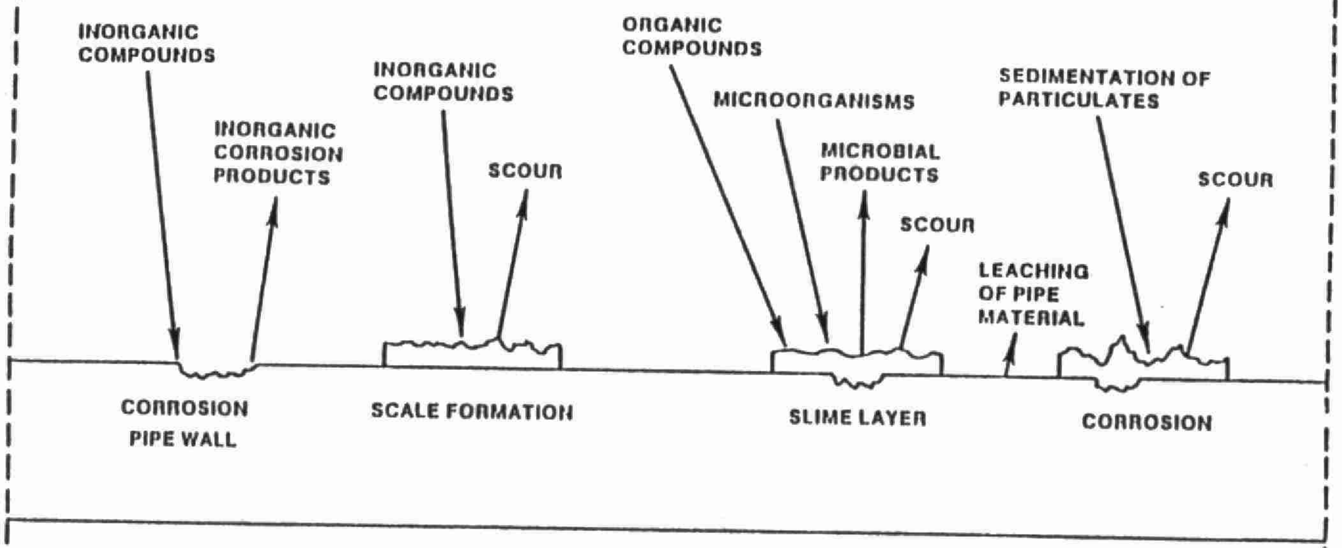


FIGURE 2. WATER DISTRIBUTION PIPE

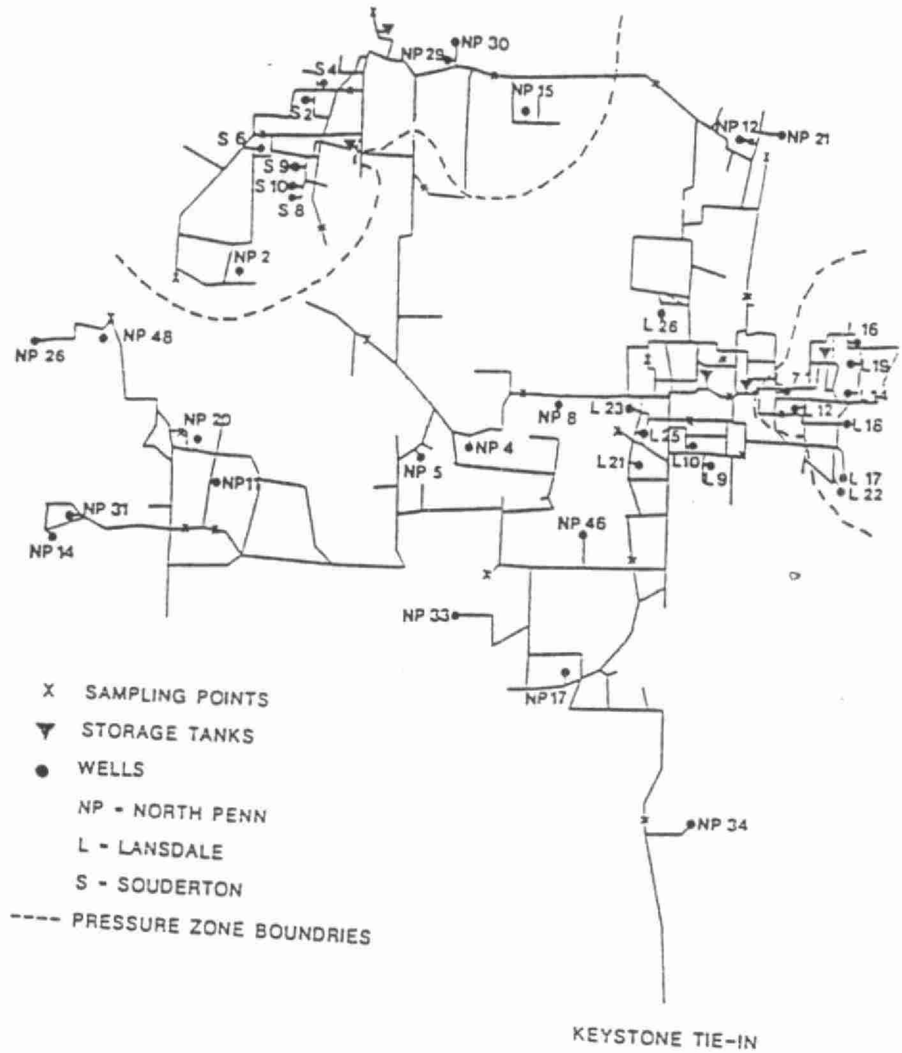


FIGURE 3. NORTH PENN WATER AUTHORITY WATER DISTRIBUTION SYSTEM

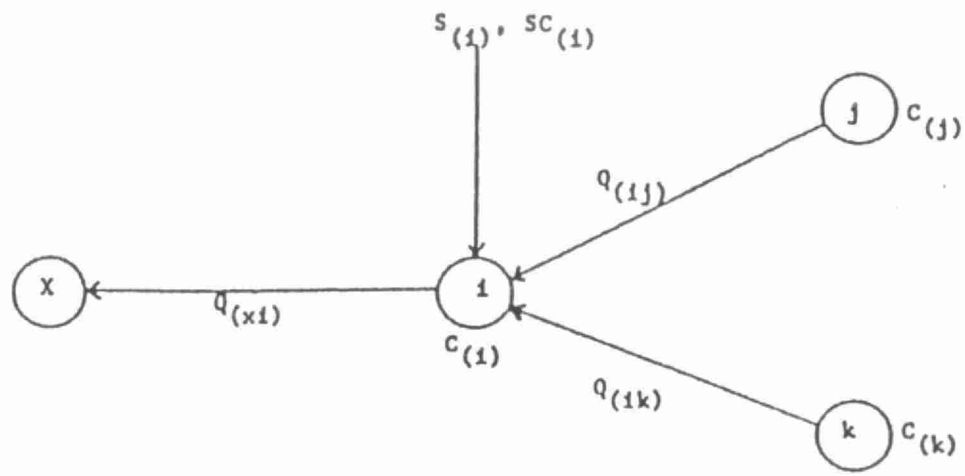


FIGURE 4. CONCENTRATION EXAMPLE

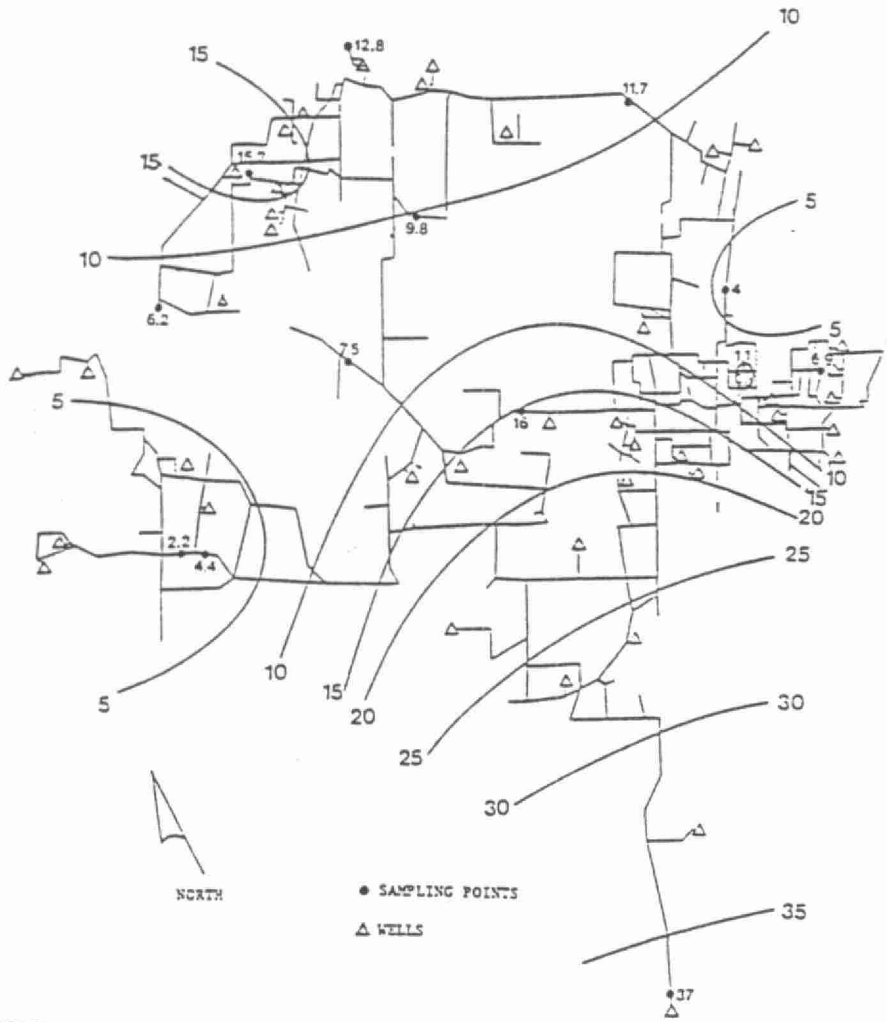


FIGURE 5. DAILY TTHM CONCENTRATION CONTOURS FOR 4-16-84 (UG/L)

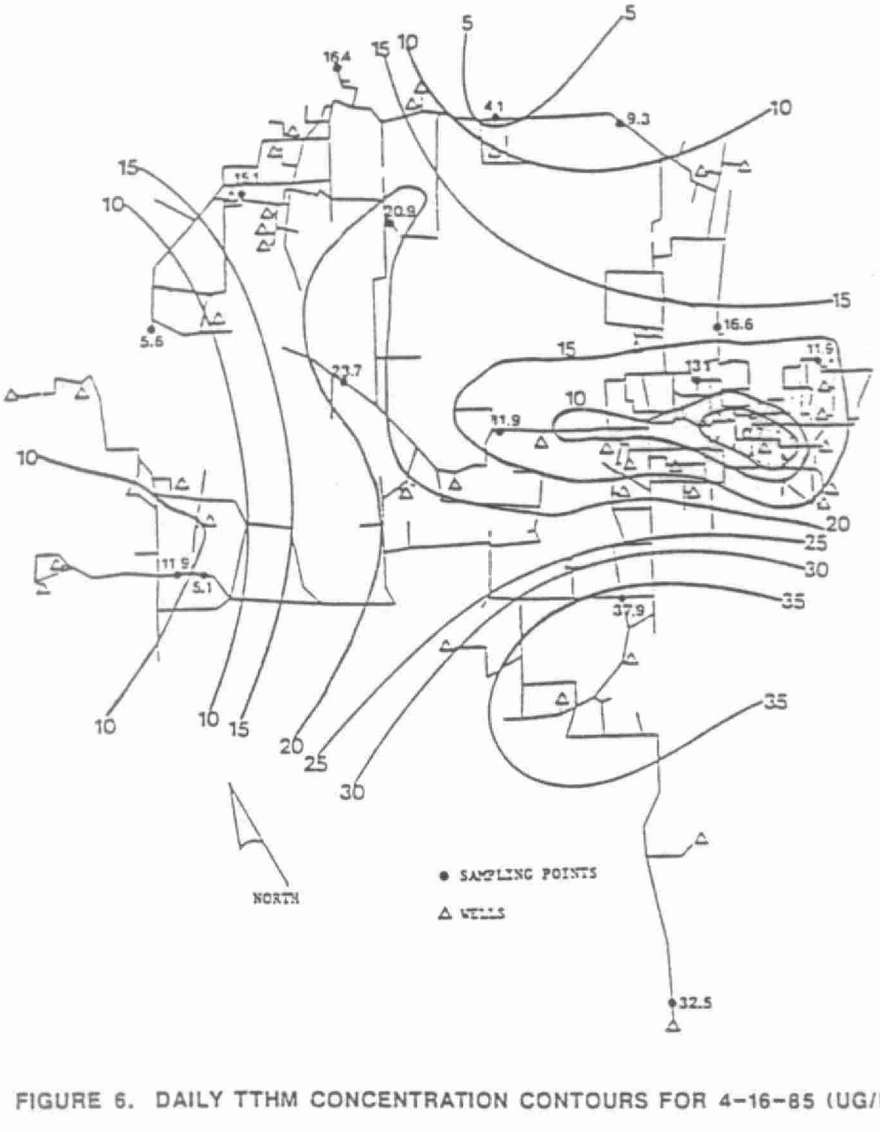


FIGURE 6. DAILY TTHM CONCENTRATION CONTOURS FOR 4-16-85 (UG/L)

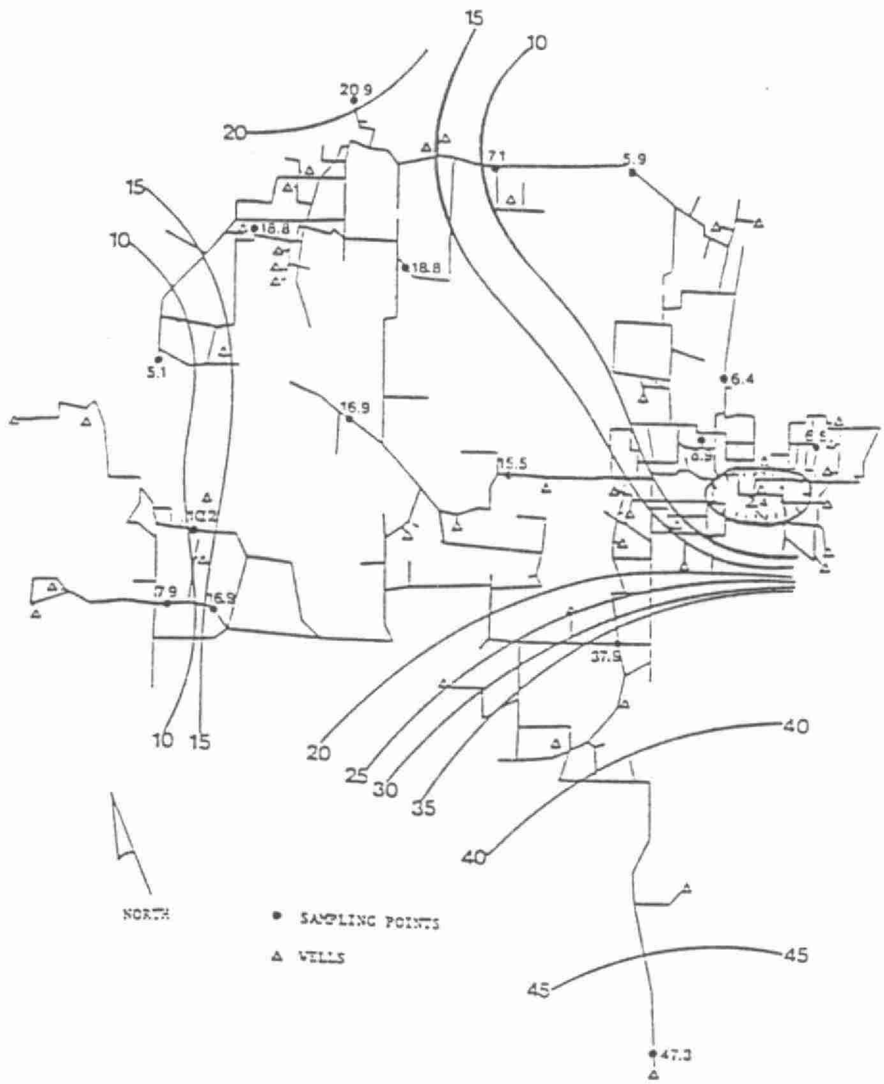


FIGURE 7. AVERAGE TTHM CONCENTRATION CONTOURS (UG/L)

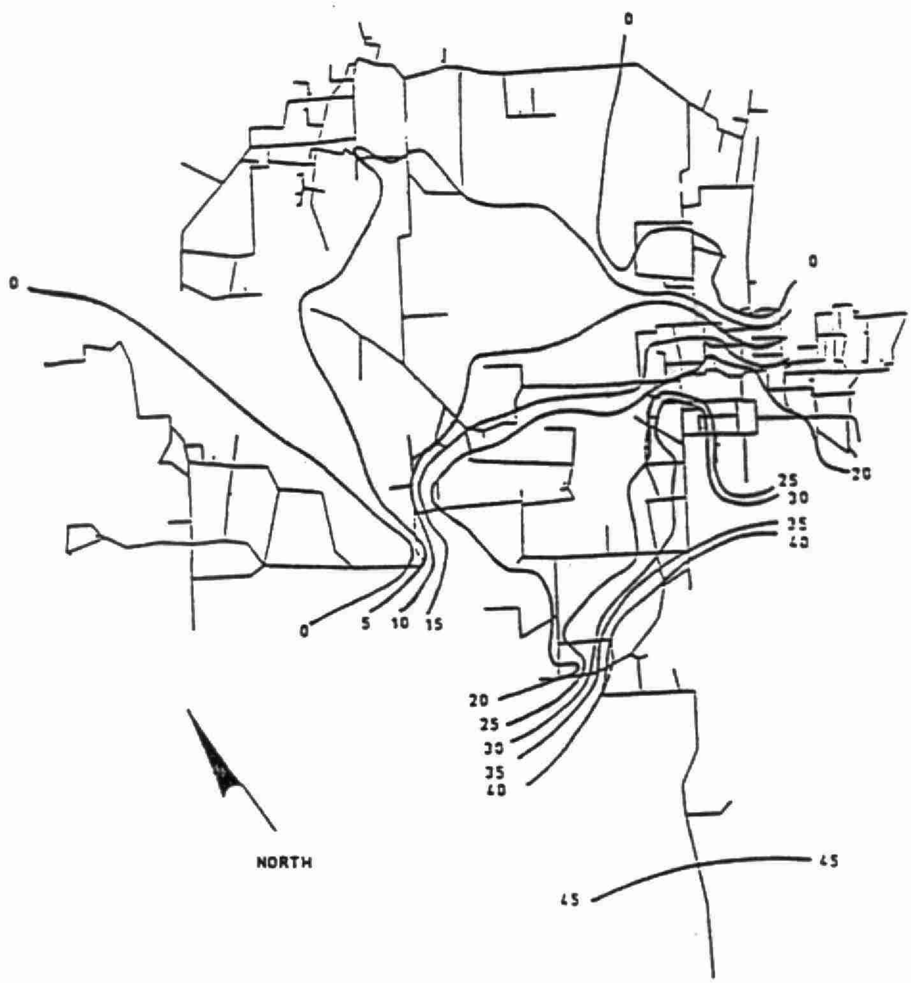


FIGURE 8. MODEL PREDICTIONS TTHM'S

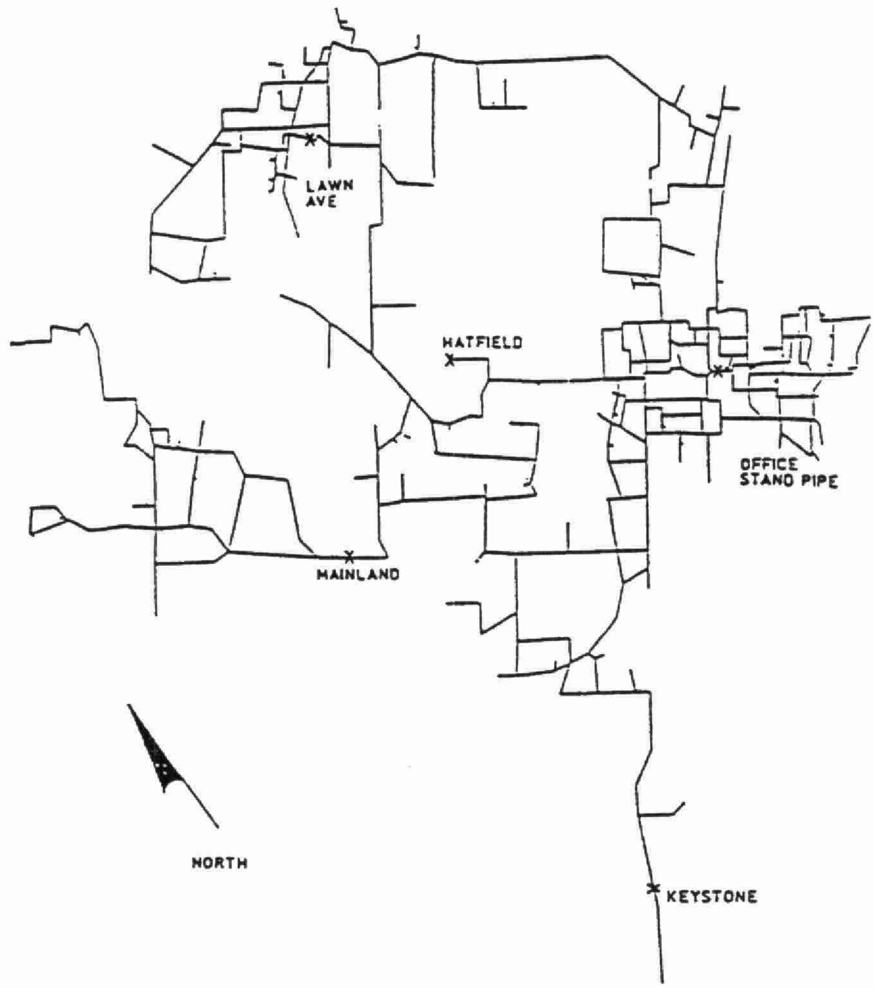


FIGURE 9. SAMPLING POINTS FOR FIELD STUDY

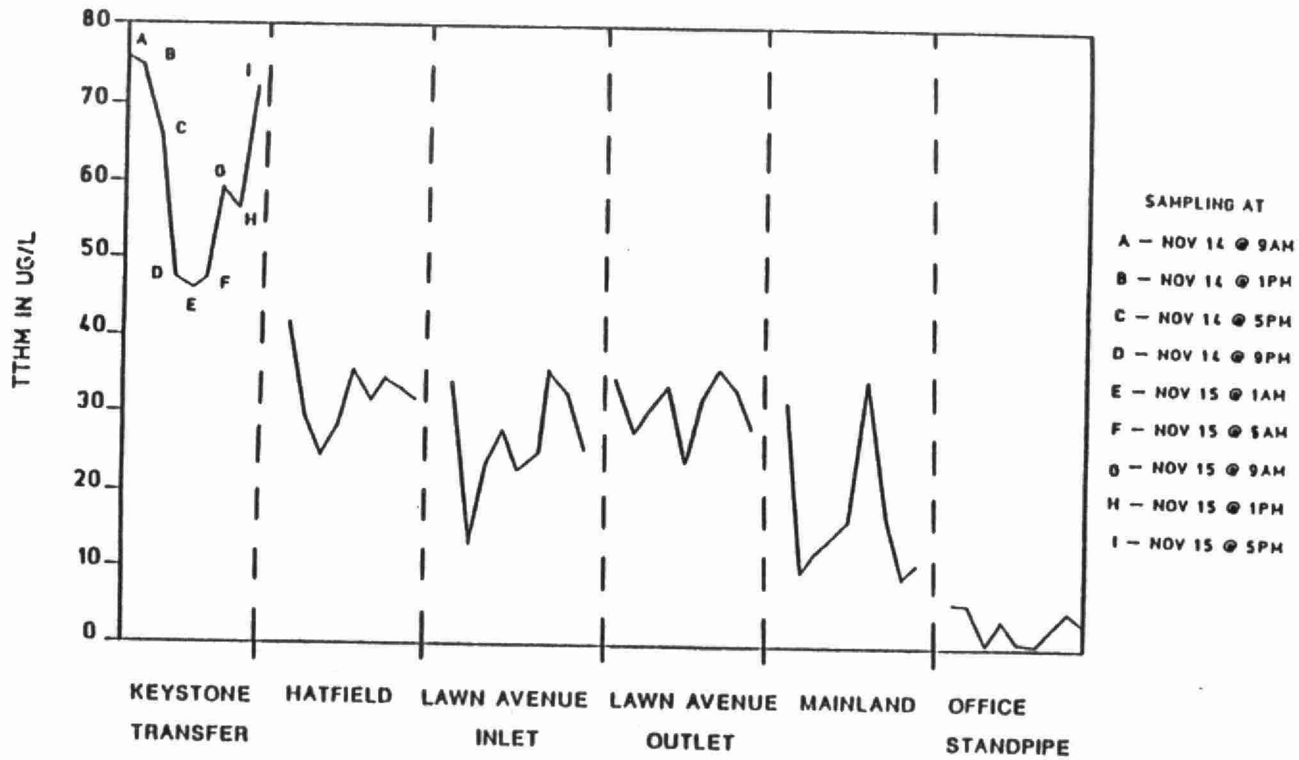


FIGURE 10. SAMPLING RESULTS FROM SIX SAMPLING STATIONS IN NORTH PENN WATER AUTHORITY

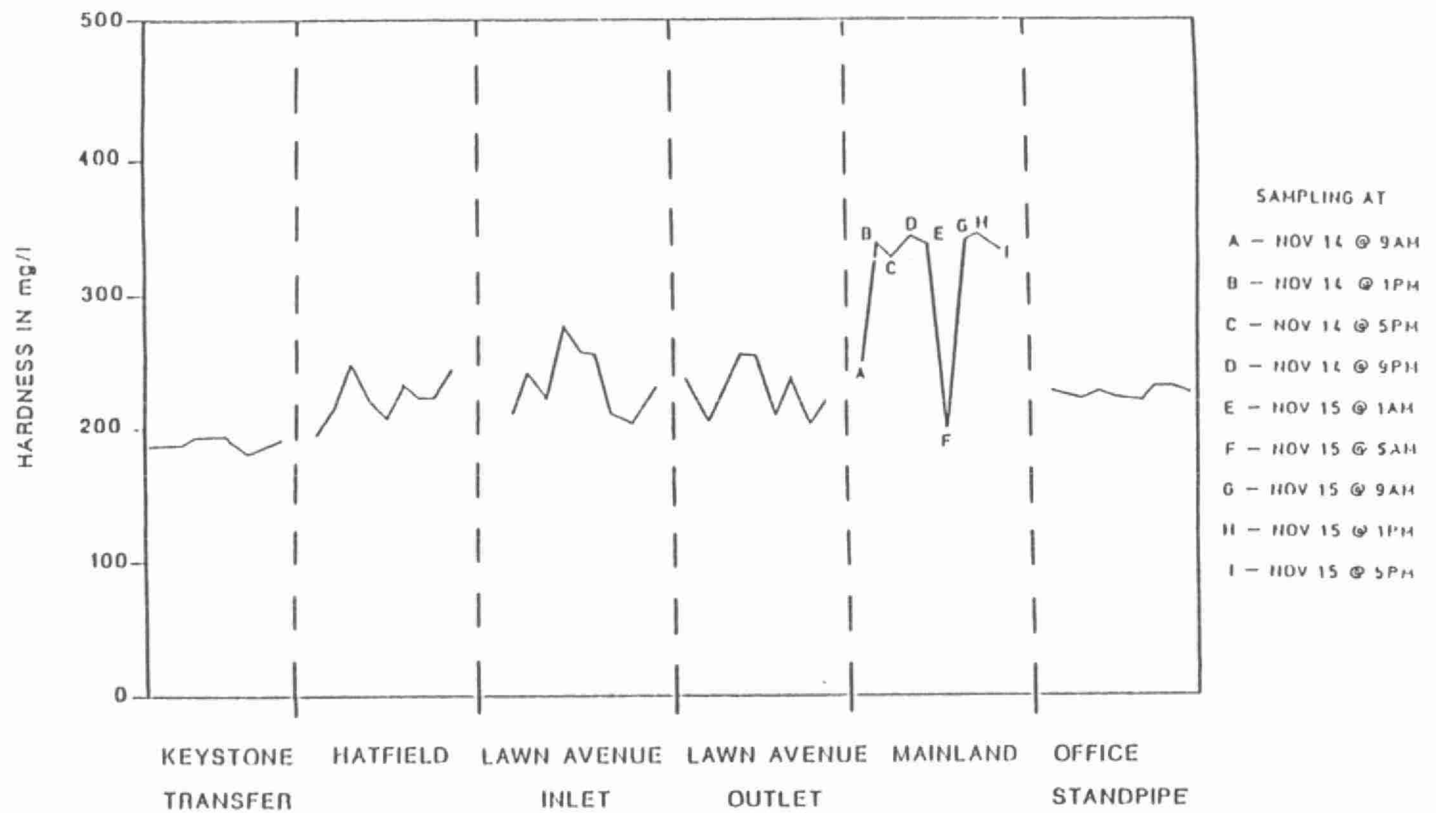
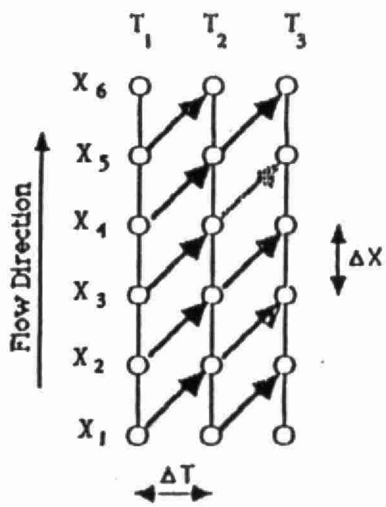


FIGURE 11. SAMPLING RESULTS FROM SIX SAMPLING STATIONS IN NORTH PENN WATER AUTHORITY



General equation:

$C_{x+1,t+1} = C_{x,t}$

where $C_{x,t}$ = concentration at sub node x at time step t

Example (see shaded arrow):

$C_{5,3} = C_{4,2}$

FIGURE 12. GENERAL ROUTING PROCEDURE FOR DYNAMIC ALGORITHM

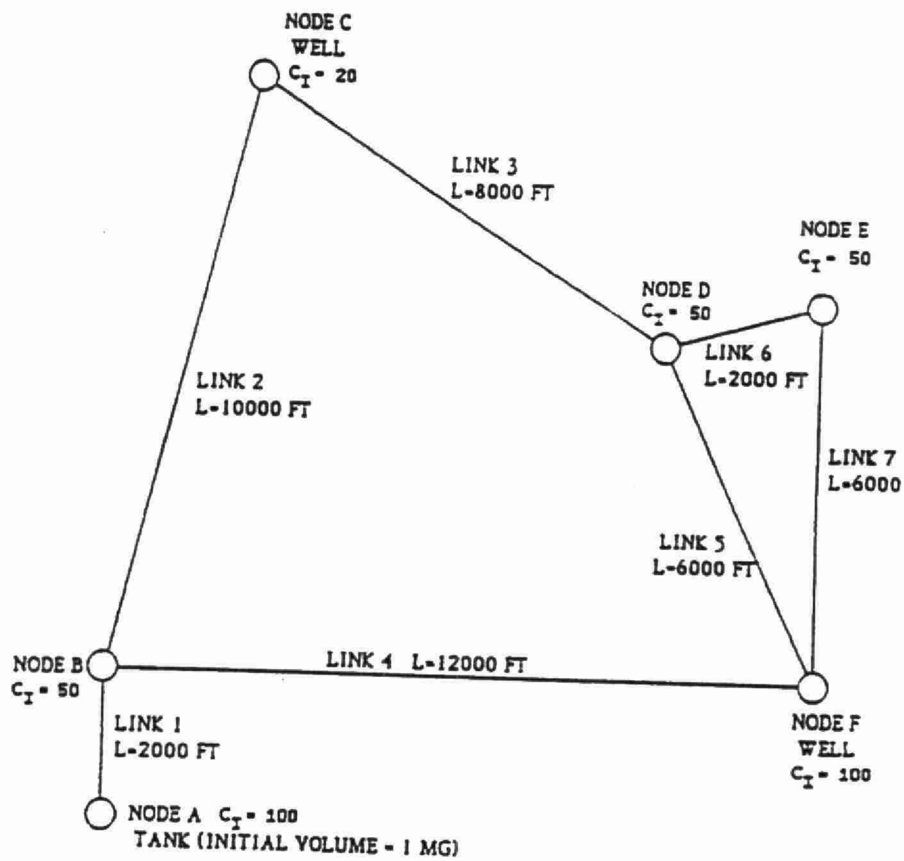


FIGURE 13. SAMPLE NETWORK

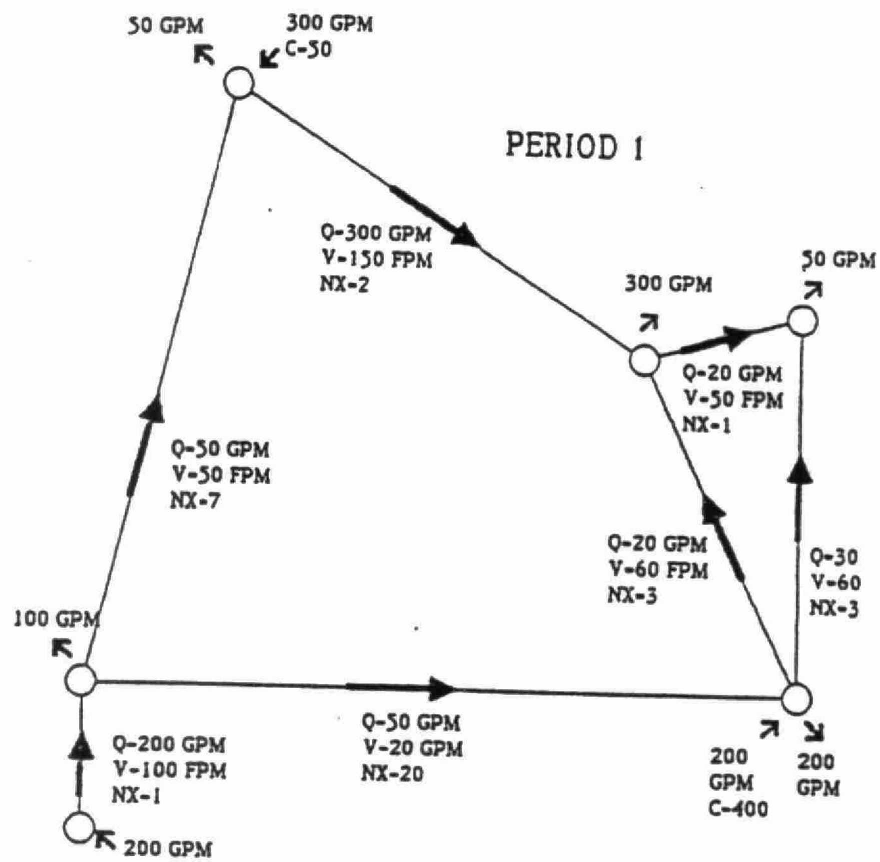


FIGURE 14. SAMPLE NETWORK WITH HYDRAULIC SOLUTION FOR PERIOD 1

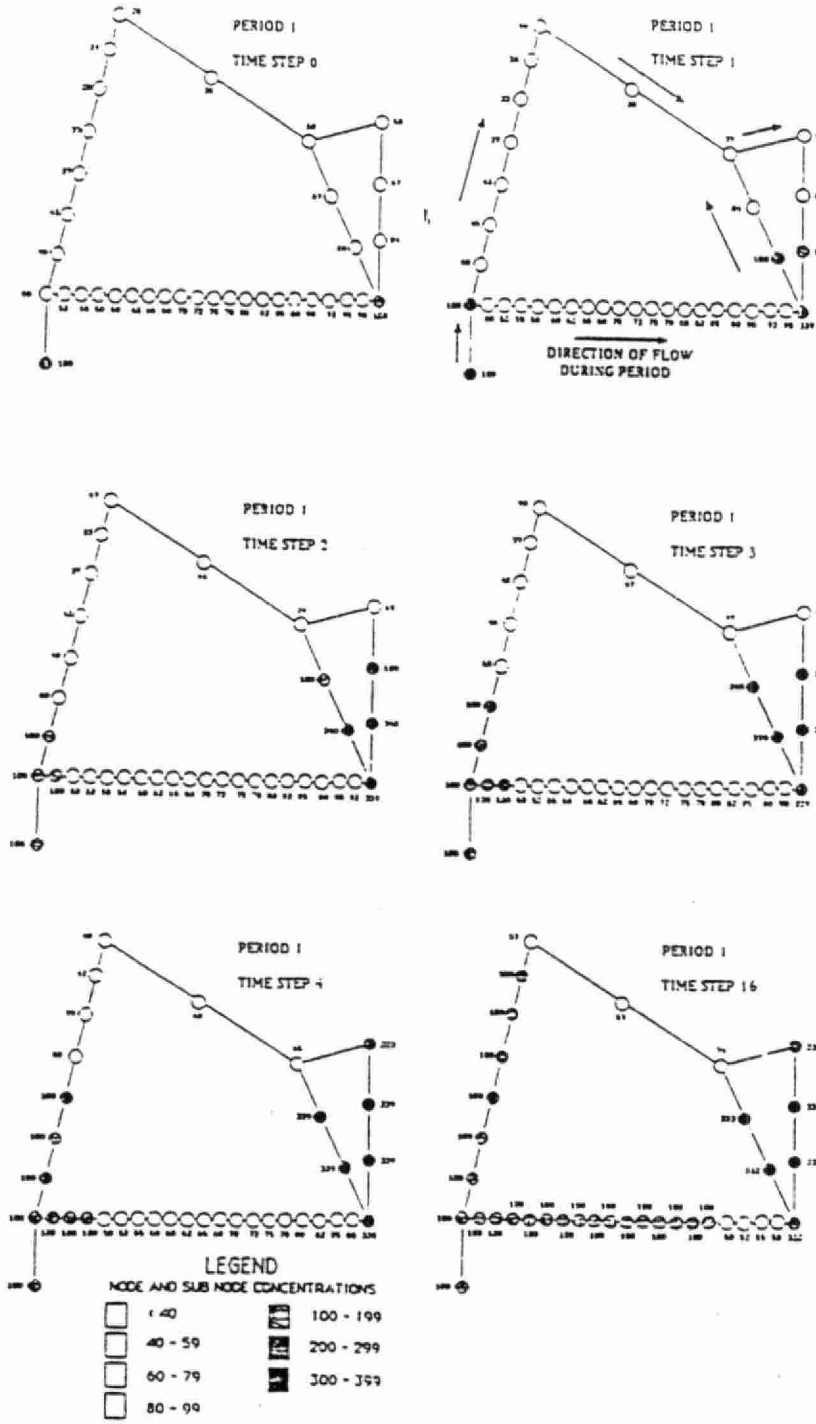


FIGURE 15. SOLUTION TO ALGORITHM FOR PERIOD 1

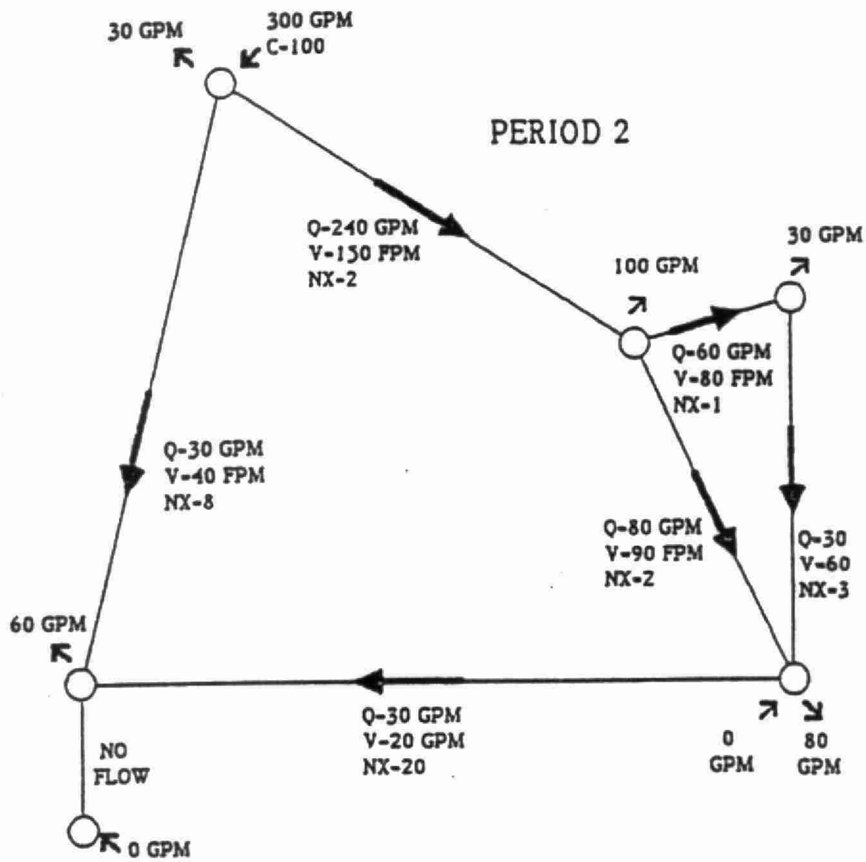


FIGURE 16. SAMPLE NETWORK WITH HYDRAULIC SOLUTION FOR PERIOD 2 AND INITIAL CONDITIONS FROM PERIOD 1

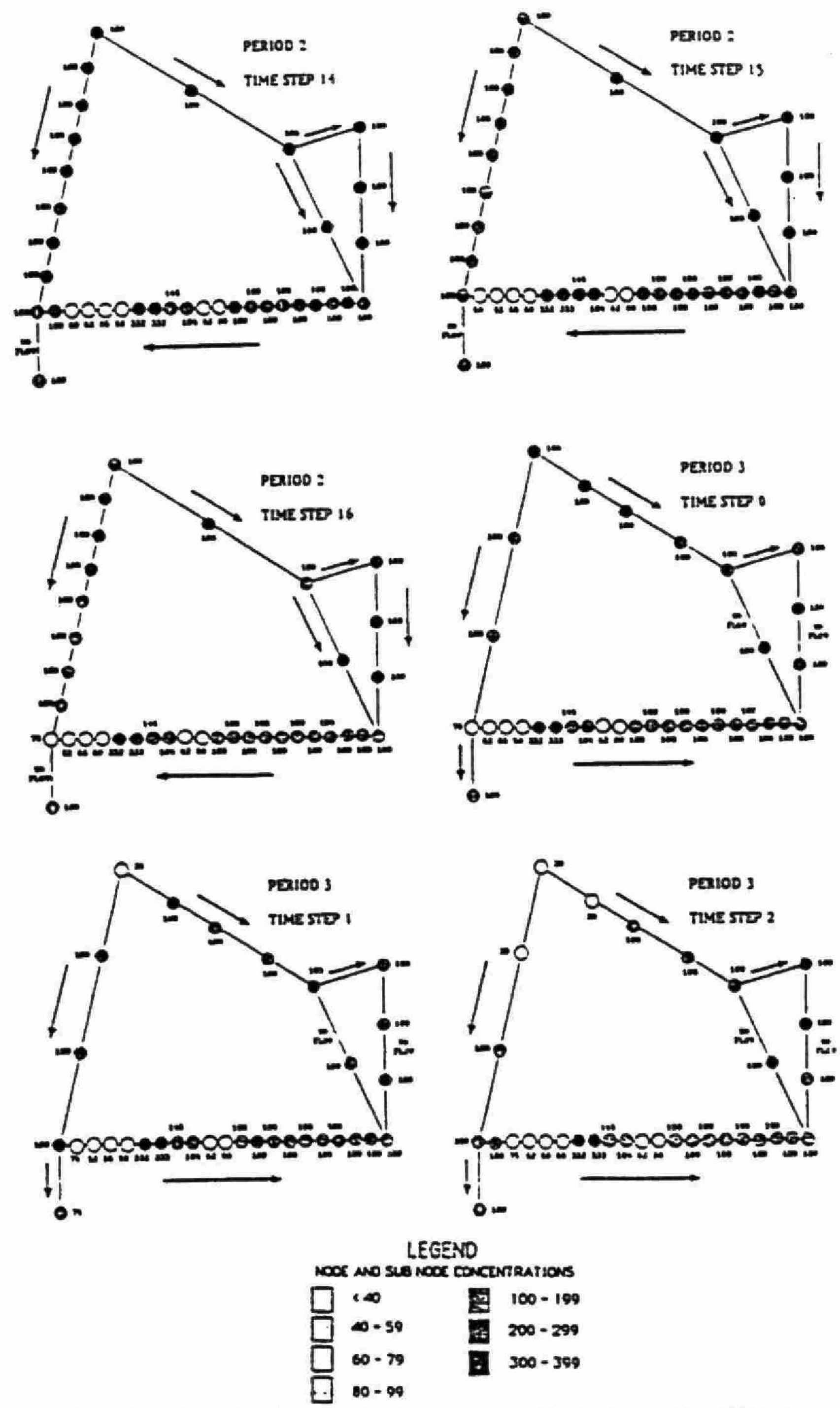


FIGURE 17. SOLUTION TO ALGORITHM FOR PERIOD 2

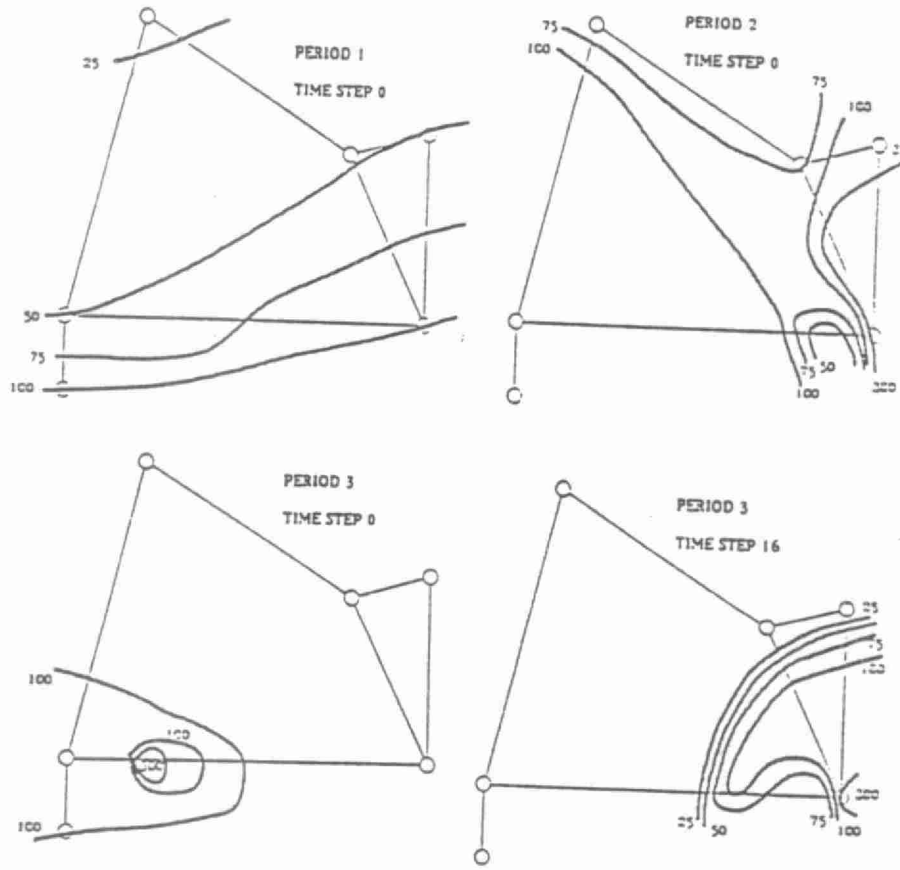


FIGURE 18. SIMULATED CONTAMINANT MOVEMENT UNDER DYNAMIC CONDITIONS

120

PROJECT DESCRIPTION

Project Title:

DEVELOPMENT OF AN INTERNAL CORROSIVITY PROTOCOL FOR WATER DISTRIBUTION SYSTEMS

Contact (name of person, organization, address, telephone):

Marvin C. Gardels, Research Chemist, Drinking Water Research Division, Water Engineering Research Laboratory, U.S. EPA, 26 W. Martin Luther King Way, Cincinnati, OH 45268, USA.
Tel: (513) 569-7217.

Project Description (Please attach a schematic diagram if appropriate):

The objective of this new project is to develop a protocol to assess corrosivity using a dual approach of expert judgments and experimental studies. A group of water supply professionals and corrosive experts from Europe and the United States will be used to develop a varied set of assessment measures to be applied in several case studies. The studies will be conducted by the University of Washington in collaboration with researchers from the Norwegian Water Technology Centre.

The EPA Mobile Water Quality Monitoring Laboratory, which the University of Washington investigators have used for the past four years in corrosion studies, will be used in this study. The lab is now capable of on-line monitoring of significant water quality factors and of determining corrosion rates by methods ranging from coupon exposure to on-line electrochemical methods. Other equipment, such as that developed in Germany for oxygen depletion measurements, will be added to the Mobile Laboratory. The old computer system has been replaced with a new IBM-PC/AT for data acquisition and processing. Several innovative techniques for corrosion measurement developed during the last project will be used on this new project.

Operating and cost data (including data on efficiency, results, etc.):

The EPA Mobile Laboratory is self-contained with analytical and corrosion measuring instruments tied into an on-board computer. Water to the laboratory is brought in through a hose attached to a hydrant and is circulated through various pipe loops and cells for analytical and corrosion measurements. Data is transferred to the computer for processing. Water flows continuously during the data acquisition and is discharged to a drain. Grab samples are taken at periodic intervals for trace metal analysis.

Place(s) of installation/application (including dates):

The Mobile Laboratory was used at several locations in the Seattle distribution system during the start up of corrosion control treatment. Other sites include Tacoma, Anacortes, Moses Lake and Ellensburg, Washington. It is presently at Everett for the first use of the IBM computer. Sites for the new project are yet to be determined.

Patent staus, if applicable:

NONE

Other information (e.g., funding source, cooperating agencies, etc.):

The Drinking Water Research Division Project Officer is Marvin C. Gardels and the project is being conducted as a cooperative agreement with the University of Washington, Seattle, Washington. The Principal Investigators at the University of Washington are Dr. John Ferguson and Dr. Mark Benjamin.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

AN INNOVATIVE APPROACH TO ELECTROCHEMICAL CORROSION RATE MEASUREMENTS IN DISTRIBUTION SYSTEMS

Steve Reiber
John Ferguson
Mark Benjamin

Department of Civil Engineering
University of Washington
Seattle, Washington 98195

The electrochemical polarization of copper, black iron and galvanized iron pipes was studied to evaluate methods of improving the accuracy of electrochemical corrosion rate measurements. A new cell configuration has been developed that utilizes pipe coupons as the test surface and simulates the conditions and flow characteristics of the distribution system. The cell can be used to map variations in the corrosion potential across the pipe coupon. A six-point polarization procedure is used to estimate the corrosion current and the Tafel slopes. Results indicate that Tafel behavior of the pipe surface varies as a function of material, exposure duration and water quality conditions.

INTRODUCTION

The principal electrochemical technique used for corrosion rate measurement in drinking water systems is the polarization resistance method, also called linear polarization. Polarization resistance methods have been widely used since 1939 when the principle was first described by Wagner and Traud (1) and then expanded upon by Stern and Geary (2) in 1957. The basic relationship derives from the modified Butler-Volmer equation (3) and assumes that electrochemical kinetics are solely a function of activation energy:

$$I_{meas} = I_{cor}[10^{(E-E_{cor})/B_a} - 10^{-(E-E_{cor})/B_c}] \qquad (1)$$

where I_{meas} is the measured polarization current that flows between the metal and the counter electrode (equal to the difference between the partial anodic and cathodic currents, $i_{o,m} - i_{r,z}$); E_{cor} is the open circuit corrosion potential (freely corroding potential); E is the potential imposed upon the metal; I_{cor} is the corrosion current that exists under freely corroding conditions and is the value being sought. It cannot be directly measured since $i_{o,m} = i_{r,z}$ at E_{cor}. B_a and B_c are fitting parameters called the anodic and cathodic Tafel slopes, respectively.

Application of this equation to a corroding surface is valid given the following assumptions: (1) no ohmic voltage drops and no concentration polarization exist; and (2) the rest potential of the corroding system is sufficiently displaced from the reversible potentials of the respective anodic and cathodic reactions (usually differences of 200 mV or greater are sufficient).

Classical polarization resistance techniques derive from the observation that Equation 1 becomes nearly linear for small values of $[E-E_{cor}]$. The derivative of current with respect to potential taken at

$[E-E_{cor}=0]$ results in the expression:

$$[dI_{meas}/dE]=2.3I_{cor}[1/B_a+1/B_c]=1/R_p \qquad (2)$$

which can be rewritten in the familiar form:

$$I_{cor}=[B_aB_c/2.3(B_a+B_c)]/R_p=K/R_p \qquad (3)$$

where R_p, the polarization resisitance, has units of ohms and is equal to the slope of the potential vs. current plot at $[E-E_{cor}=0]$. The factor K is an explicit function of the Tafel slopes.

Equation 3 offers a simple and direct means of solving for I_{cor} if an accurate estimate of the Tafel slopes is available. Commercial corrosion rate meters make use of this equation by employing an internal "hard wired" value for K and measuring the polarization resistance at a specific potential offset from E_{cor}, usually less than 20 mv. While these meters offer simplicity and speed, absolute accuracy suffers because the electrochemical parameters cannot be adjusted to fit the different conditions of the different cells, or the changing conditions of a given cell over time (4, 5).

Commercial polarization resistance instruments are produced in several electrode configurations. Perhaps the most popular design is a three electrode system manufactured by Petrolite Corporation (Houston Texas). The three electrodes in this design are made from the metal of interest and have a cylindrical geometry. Each corrodes freely and establishes its own corrosion potential (E_{cor}). In operation, one serves as the reference electrode, one the counter and the remaining as the test electrode. The difference in freely corroding potential between the reference and the test electrode is measured, and an offset potential (10 mV) in either the anodic or cathodic direction is applied to the test. After a preset equilibration time the impressed current is measured and converted to a corrosion rate using the relationship previously described. This simplified technique is appropriate for qualitative assessments of corrosion conditions and for determination of the relative rates of corrosion in similar system.

The purpose of this paper is to report on the development of new hardware to aid in the electrochemical measurement of corrosion rates on plumbing surfaces. The goals of this program were fourfold:

1. Design a simple polarization cell and associated instrumentation that can be reproduced easily in numerous laboratories.

2. Utilize actual plumbing materials (black iron, copper and galvanized iron pipe sections) as the corrosion measurement surface.

3. Develop a cell geometry that reflects the hydrodynamics of pipe flow and its impact on the corrosion surface.

4. Develop polarization technniques that can determine Tafel behavior of the corrosion surface under the specific water quality and pipe surface conditions of interest.

US-76

EXPERIMENTAL APPARATUS AND MATERIALS

Polarization Cell and Electric Circuit

A cross section of the polarization cell developed for this study is presented in Figure 1. As in a typical polarization assembly it consists of test, reference and counter electrodes, but the configuration and geometry of this cell is unique. Cell operation calls for axial water flow through the test electrode section, which can be adjusted to simulate pipe flow velocities or Reynolds numbers. The test electrode itself is made from sections of water pipe, either 1/2 inch black iron or galvanized pipe, or 5/8-inch type K hard copper tubing. The counter electrode penetrates the axial center of the cell along its length, and is thus equi-distant from all points on the test electrode surface. This prevents distortions in the current flow during polarization extremes, even when ohmic resistance may be significant. The reference electrode is a Ag/AgCl electrode encased in a narrow, flexible polyethylene stem. A large ceramic frit junction fits into the end of the stem and can be recessed any desired distance. The junction frit is porous and has a high leak rate, ensuring an exceptionally stable reference voltage. A principal advantage of the flexible electrode is that the junction can be positioned at any location in the polarization cell. This is particularly useful for studying the variation of corrosion potential across the test electrode surface.

A modified RDE2 Potentiostat (Pine Potentiostats, Pine, Pennsylvania) is used to conduct the polarization scans. Analog output from the potentiostat is converted to digital form by a Keithley Series 500 Data Acquisition System (Keithley Co., Cleveland, OH.). Data is then transfered to an IBM-PC based microprocessor for statistical analysis, graphing and storage.

For determination of distribution system corrosion rates the polarization cell, with the appropriate test electrode, can be mounted in a flow-through loop and continuously monitored. It may also be mounted in a closed loop where precise water quality conditions are maintained, or where water quality transients can be induced and their effect upon corrosion rates monitored. Figure 2 is a schematic of the closed loop recirculation system used in this study. Mechanisms are provided to control temperature, flow rate and dissolved gases. Chemical addition ports for inducing transients during monitoring, as well as sampling ports to test for the release or buildup of corrosion products, are provided. Instrumentation is installed for the continuous monitoring of pH, temperature, conductivity and dissolved oxygen.

Materials and Specimen Preparation

Test electrodes (pipe coupons) are machined from common plumbing materials. These include half-inch black iron pipe (ASTM A 120), half-inch galvanized iron pipe (ASTM A 120-82), and hard copper tubing (type K, ASTM B 88). However, the larger inside diameter of the copper tubing produces a fluid contact area substantially greater than the other types of pipe. The larger surface area also requires a polarization current beyond the capacity of the potentiostat, hence thick-walled copper tubing with a narrower inside diameter was used in some parts of this investigation. Figure 3 presents a photograph of typical black iron,

galvanized iron and copper test electrodes used in this study. Note that the ends of the electrodes are lathe cut to ensure a smooth and flat finish that seals tightly against the neoprene gaskets of the polarization cell. Corrosion occurs on only the interior surface of the coupon. The test electrodes, or coupons, are cut to a nominal length of 4 cm. Black iron and galvanized iron have an interior surface area of 18.5 sq. cm., and the thick walled copper tubing presents an interior surface of 12.5 sq.cm. After machining the coupons are polished, then stamped with an identification number and given an exterior coating of clear acrylic.

Considerable work has gone into the development of new pipe coupon preparation and weight loss measurement techniques. These techniques differ substantially from ASTM D 2688-83 Method C - "Machined Nipple Test" (6) or ASTM D 2688-83 Method B - "Coupon Test" (7). The new techniques utilize soft, high-speed wire brushes and felt polishing tools to mechanically prepare the coupon corrosion surfaces. This reduces preparation time and increases the overall accuracy of the weight loss measurement when compared to the acid dissolution and chemical rinse techniques used in the more common coupon preparation standards. Details will be reported in a subsequent paper.

Comparison of electrochemically measured corrosion rates with weight loss measurements on metal coupons was used to validate cell performance. Weight loss measurements are made by placing a sleeve containing as many as ten coupons (identical to the the test electrode) in-line with the polarization cell. Coupons are butted end-to-end and separated by neoprene washers (see Figure 4). The configuration is advantageous because of the high sample density and the ability to easily retrieve individual coupons.

Because the coupons are relatively small, a larger number can be used, giving a more accurate statistical estimate of corrosion rate than the larger, single machined nipples used in ASTM D 2688-83. As has been demonstrated in other reports, weight loss estimates of corrosion rates vary dramatically (by as much as twofold) even for identical samples exposed to similar conditions (8, 9). Much of this is due to the difficulty of cleaning and preparing the corrosion surfaces. These errors can be reduced by testing several coupons and using careful mechanical surface preparation techniques.

Table 1 presents the results of a typical weight loss test conducted in Seattle tap water. The coupon exposure period was 24 hours, median pH was 7.7 with a temperature of 15 degrees-C, conductivity averaged 55 umhos/cm, dissolved oxygen was saturated at 10 mg/l, and flow through the sleeve was maintained at a velocity of 1 ft./sec.

At the 95% confidence level the precision of the corrosion estimate is approximately 25% of the average weight loss measurement. Part of the variation can be explained as the actual difference in corrosion rates on different coupons due to surface and material variations. Still, a large part of the variation is probably due to the coupon preparation technique. Because this was an extremely short exposure with minimal weight loss, the contribution of preparation technique to the imprecision is magnified. Extended exposure produces proportionally higher weight loss, thus increasing the overall analytical precision. Precision of weight loss tests with durations in excess of one week improved to 20 percent or less.

EXPERIMENTAL PROCEDURES AND RESULTS

Surface Potential Measurement

E_{cor} is the freely corroding electrochemical potential that a surface assumes (with respect to the reference electrode) in the absence of an impressed current. Because the test electrode surfaces of this study are relatively large, significant spatial variations in E_{corr} exist. As described by Uhlig (10), the freely corroding surface takes the form of multiple "local-action cells" where the respective oxidation and reduction half-cell reactions occur. As will be demonstrated, large variations in potential may exist between different "local-action cells". Also, positive and negative electrode areas interchange and shift from place to place as the corrosion reactions proceed. The more negative cells form the anodic sites where the metal is oxidized. These are often covered by a porous layer of corrosion scale. The more positive cathodic cells form the sites where the corresponding reduction of oxygen occur. Such sites are usually clear of corrosion products.

Of the three materials studied, the variation of surface potential was the most pronounced on black iron coupons. The variation was enhanced because of the tendency of these surfaces to undergo pitting type corrosion under the water quality conditions tested (11). Conversely, with few exceptions copper surface corrosion under typical distribution system conditions is uniform (12). The zinc coating on galvanized pipe is also significantly more uniform in its initial corrosion patterns than black iron. However, once the galvanized layer has been penetrated, it is subject to extreme pitting (11).

The distribution of anodic and cathodic sites on metal surfaces and resulting variations in corrosion potential has been explored by several authors (8, 13). The experience of this study has been that the more nonuniform the corrosion pattern the larger the surface variations in E_{cor}. With the flexible reference electrode and the rotating cap of the polarization cell it is possible to scan the surface of the test electrode and map the corrosion potential variation. Figures 5, 6 and 7 present, respectively, a surface scan over a one cm. wide circumferential band of an iron, galvanized iron and copper pipe coupon. Each coupon was exposed for approximately 96 hrs. to a 1 ft/sec velocity of Seattle tap water (temp = 15 ^{o}C, conductivity = 55 umhos/cm, dissolved oxygen = 10 mg/l, pH = 7.8).

Figure 5 clearly shows the dramatic variation in E_{cor} associated with the nonuniform iron corrosion. Although this coupon had been exposed for only 96 hours, distinct pitting sites had been initiated, accompanied by an overlying iron oxide scale. The deep valleys of the scan correspond to these areas, while the flatter higher potential areas represent the bulk of the coupon surface that remains free of scale covering. The pits at this exposure duration are generally about two millimeters in diameter with a penetration depth of less than 0.1 mm. The scan, however, indicates that the area of influence around the pit is substantially larger than the pit itself.

The uneven distribution of the scale distorts the measurements of polarization resistance (dV/dI) used to characterize the polarization behavior of the coupon. When the distribution of corrosion scale is uneven, it is often necessary to make multiple readings at different surface locations. Comparisons of electrochemical and weight loss

measurements indicate that extreme polarization resistance measurements on the pitting surfaces, either high or low, should be discarded. Measurements taken on the more cathodic areas of the coupon will "cluster" around an average value that accurately reflects the corrosion rate and associated electrochemical parameters.

This averaging technique works satisfactorily on iron coupons where the corrosion scale is relatively thin (less than 1 mm). However, experience has shown that this is unsatisfactory on aged black iron coupons with thick scales, or scales that form large patches as opposed to a distribution of smaller discrete pits. The correlation of the electrochemical corrosion measurement technique compared to weight loss measurements decreases dramatically with formation of these conditions.

The potential scans on copper and galvanized iron (Figures 6 and 7) show a more stable surface E_{cor} than iron. The uniform nature of their corrosion process and scale deposition explains this difference. On these surfaces polarization resistance measurements show only slight spatial variation, and since both copper and zinc scales are generally thinner than iron scales, the measurement distortion is not a problem regardless of coupon exposure time or scale growth.

General Polarization Measurements

In general, corrosion rates measured in water distribution systems are an order of magnitude lower than those observed for iron in seawater, or the down-hole tooling of an oil drilling rig. Most electrochemical measurements in these environments deal with corrosion current densities measured in milliamps/cm^2., while current densities on common water distribution plumbing materials are more likely to be in the microamp/cm^2. range. It is usually easier to make an electrochemical measurement on a rapidly corroding system, not only because the current densities are higher, but also because a rapidly corroding surface returns more quickly to its freely corroding condition following the application of a polarizing current.

Because distribution system corrosion is relatively low, maintaining the freely corroding condition of the test electrode surface is crucial for an accurate measurement. This task is complicated because the freely corroding surface is readily affected by mechanical action, such as scale removal, or by electrochemical actions that favor either the anodic oxidation or the cathodic reduction processes. This means that polarizing the surface by impressing a current density of several milliamps/cm^2, as would be the case for a rapidly corroding surface, is not appropriate, since it alters both the physical and electrochemical character of the electrode surface. The problem is further complicated by the drift of the baseline E_{cor}. As demonstrated by surface potential scans (Figures 5, 6 and 7), large spatial variations in surface potential are possible on metal plumbing surfaces, and experience indicates a temporal component to this variation. An individual site may show a potential shift of + or - 10 mV within a five minute period. Shifts as great as 50 mV in a day have been observed, especially on iron. This supports the hypothesis that anodic and cathodic regions can be constantly in motion, establishing a "dynamic" surface equilibrium where the favorability of specific half-cell reactions change as the corrosion process proceeds. Because anodic and cathodic sites are constantly shifting, measurement of polarization resistance at a particular point on the surface should be completed quickly before the baseline E_{cor} (from which the polarization offset is measured) can shift substantially.

Application of a polarizing current generally increases the baseline drift since it tends to redistribute the anodic and cathodic sites (14). If the baseline is not stable, the polarization offset, and hence the polarization resistance, cannot be accurately measured. This, combined with the sensitivity of the corrosion surfaces to perturbations caused by impressed currents, mitigates against the use of the usual anodic and cathodic continuous polarization scans (15). Instead a six point polarization offset procedure similar to those suggested by Danielson et.al. and Jankowski et.al. (16, 17) is used. The electrode is polarized to offsets of 20, 40 and 60 mV in the anodic direction, and -20, -40 and -60 mV in the cathodic direction. Each polarization step is completed within a two minute span, hence the oppotunity for baseline drift is minimized. Because the magnitude of the polarizations are small the potential disturbance to the character of the freely corroding surface is lessened, yet the perturbations are large enough that the impressed current can be accurately measured. Baseline E_{cor} is measured both before and after each polarization to ensure that drift is minimal. The polarization is repeated if drift produces an error greater than 10 percent of the target offset.

Electrochemical parameters are calculated from the polarization data by fitting each point to the modified Butler-Volmer equation (Equation 1) and selecting Tafel slopes that give the least overall error between observed and predicted polarization currents. The procedure is summarized in the flow diagram of Figure 8. A BASIC language program has been developed to speed the iterative series of cumbersome calculations. In essence, it is a brute force approach that tests every feasible combination of anodic and cathodic Tafel slope and ultimately selects the pair that gives the best fit. In this sense it is similar to the earlier POLCORR program (18). After establishing the appropriate search boundaries and iteration increments a corrosion current is calculated using the Leroy model (19) and the first selection of Tafel slopes. Leroy's model is a statistical approach that is useful for predicting the corrosion current density from a limited set of polarization data assuming a given set of Tafel slopes. It takes the form:

$$I_{cor} = \frac{\sum_{j=1}^{n} [I_j(10^{(E_j-E_{cor})/B_a} - 10^{-(E_j-E_{cor})/B_c})]}{\sum_{j=1}^{n} [(10^{(E_j-E_{cor})/B_a} - 10^{-(E_j-E_{cor})/B_c})^2]} \qquad (4)$$

The corrosion current and Tafel slopes are applied in equation 4 to give the predicted polarization currents for the respective polarization offset. If any one predicted value shows an error greater than some arbitrary cut-off (usually 5 - 10 percent of the observed value) the set of predictions is rejected. The Tafel slopes are then incremented by the preset amount and the calculation restarted. If all predicted values fall within the maximum allowable error the values are stored along with the sum of the square of the total error. Tafel slopes are then incremented and the calculation proceeds until all possible combinations established within the original limits have been tested. Selection of the actual Tafel slopes uses the minimum sum of the squares of the errors as its goodness of fit criteria.

rocedures described appear cumbersome and time consuming, even for a computer based solution. However, the task is simplified by the insensitivity of equation 1 to minor changes in the Tafel parameters, and the well documented range of feasible Tafel slopes for each metal of interest. Because of insensitivity the incremental adjustments to the Tafel slopes need not be less than 10 mV. Choosing a smaller value may find a marginally better fit, but such efforts are not justified considering the precision of the actual polarization measurements. A large body of experimentally determined Tafel slopes for each metal has been catalogued by the National Association of Corrosion Engineers (19). These data will generally bracket a feasible solution. An iteration boundary of plus or minus 100 mV around the anticipated value is usually sufficient to locate a satisfactory fit.

Figures 8 and 9 are Evans diagrams constructed from polarization data collected on black iron coupons exposed to the Seattle distribution system for 24 hrs. and 7 days, respectively. The lines of best fit (polarization curves) resulting from the parameter estimation technique described above are overlaid on the six measured polarization points. In this case the maximum single error between measured and predicted values is less than 5 percent of the measured. It is generally possible to find a fit that falls within an error range of 5-10 percent. The dashed lines intersecting at E_{cor} are extrapolations of the predicted Tafel slopes from the linear region of the polarization curve. The current density at the point of intersection represents the current density of the freely corroding surface.

Figures 10 and 11 present Evans diagrams of measured and predicted polarization values derived from copper and galvanized iron surfaces exposed for 7 days to the Seattle distribution system. In both cases the analytical approach was the same as for the black iron examples. Table 2 summarizes the parameters derived from the four polarization examples and compares electrochemically measured corrosion rates with weight loss estimates of corrosion rates made on five coupon sets exposed to identical conditions for similar durations. Corrosion current densities are converted directly to a penetration rate by applying Faradays' law:

$$\text{Corrosion Rate (uM/yr)} = I_{cor}[3.21(\text{eq.wt.})/g] \qquad (5)$$

Where g is the specific gravity of the corroding metal and the equivalent weight represents the gram wt. of metal oxidized by the transfer of one equivalent of electrons.

DISCUSSION

Accuracy of Corrosion Measurements

Very little literature is available attesting to the accuracy of any analytical technique for corrosion rate measurements in water distribution systems. Discussion of linear polarization measurements by the National Association of Corrosion Engineers (20) speaks of predicted values being within one to twofold of actual corrosion rates. Weight loss measurements can be equally inconsistant (8), with confidence limits that are only slightly better. Even ASTM standards are reluctant to state an acceptable level of precision because of the large variability encountered between systems. By contrast, the examples of Table 2 come within 25 percent of weight loss measurements and yield additional information about the electrochemical processes. The hardware and analytical techniques described in this paper offer improved accuracy for corrosion measurements on plumbing materials exposed to tap water. The accuracy approaches that necessary to distinguish between the more subtle effects of various chemical corrosion inhibitors, or to assess the effects of minor water quality changes.

Our experience has been that good correlation of the electrochemical technique with weight loss measurements can be readily achieved on the uniformly corroding surfaces of copper and galvanized iron coupons. However, surfaces that exhibit thick or extremely patchy scale, such as well aged black iron coupons, severely complicate the measurement of surface potential and polarization resistance. The spatial averaging technique described earlier is an incomplete resolution to the problem that is only appropriate at the incipient stage of pit and scale formation. Exposure periods of as little as 30 days in some aggressive waters may produce extremely pitted surfaces with abundant scale that cannot be evaluated in this fashion.

Surface Potential and Pitting

As demonstrated, the polarization cell is also useful in mapping the surface potential of the corroding metal coupons. For corroding iron, the anode and cathode reactions can be traced to specific areas of the metal surface. The surface scans define these areas by their relative potentials. Often, the extreme anodic sites represent well-defined or incipient pits. Pitting corrosion is generally a more serious problem for black iron pipe than is uniform corrosion, and often failure due to pitting determines the useful service life. Hence, penetration measurements based on an assumption of uniform corrosion do not yield useful information about the critical processes that may be occuring. Furthermore, pit formation and scale growth appear to impair the accuracy of polarization measurements and make estimation of even a uniform penetration rate (weight loss) imprecise.

The ability of the polarization cell to map the pitting sites, as well as measure the site specific response to an impressed current, may offer a means of measuring pitting penetration rates. Investigation of this possibility is a future goal of the project.

Pipe Surface Electrochemistry

In order to accurately assess corrosion rates, a reasonably accurate estimate of the basic electrochemical kinetic parameters (Tafel slopes) is necessary. The examples of Table 2 demonstrate how these parameters differ from metal to metal, as well as between coupons of the same metal under slightly different conditions. Clearly, the assumption that one set of parameters, or for that matter a single "hardwired" constant, can be applied to a variety of electrodes, may lead to serious errors in the corrosion rate estimate.

It is not surprising that substantial differences in electrochemical kinetics exist between different metals, or the same metal for different exposure periods. That a substantial difference can develop on different parts of the same metal surface exposed to a constant water quality is less intuitive and must be borne in mind when interpreting distribution system corrosion rate measurements. The variation demonstrated for black iron surfaces in Table 2 is typical of the difference observed between fresh and relatively aged surfaces. Smaller differences of this type have been observed on copper electrodes as well.

CONCLUSIONS

1. The flow-through polarization cell offers greater accuracy than typical linear polarization instrumentation for corrosion rate measurement in distribution systems. The improvement results from the use of plumbing material as the test electrode surface and the inherent flexibility of a system capable of surface potential scans and determination of fundamental electrochemical kinetic parameters.

2. Over time, exposure to distribution water changes the surface conditions of plumbing materials and can alter the values of electrochemical parameters (Tafel slopes) that determine corrosion kinetics. Corrosion rate measurements require accurate estimates of Tafel behavior relative to the specific conditions and duration of the metal's exposure. A six-point polarization technique coupled with a program designed to select Tafel values that most closely fit the predicted to the observed polarization values has worked satisfactorily.

3. Corrosion surfaces formed in the distribution system are sensitive to both mechanical and electrochemical disturbances. Polarization in excess of 100 mV in either direction rapidly alters the freely corroding surface of black iron coupons and makes accurate corrosion rate measurements difficult. Galvanized iron and copper surfaces are affected in a similar manner, but to a lesser extent.

4. The nonuniform nature of corrosion on black iron coupons usually requires several polarization measurements at different locations to characterize polarization current. A simple averaging of values gives good results for clean surfaces and surfaces with only minor pitting. Heavy or patchy scale conditions distort both the surface potential and subsequent polarization current measurements, reducing the accuracy of the result by several fold.

AUTHORS

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NOMENCLATURE

B_a = Anodic Tafel Slope (mV/decade of polarization current)
B_c = Cathodic Tafel Slope (mV/decade of polarization current)
I_{meas} = Measured Current Density Impressed upon the Test Electrode Surface ($uAmps/cm^2$)
I_{cor} = Corrosion Current Density ($uAmps/cm^2$)
E_{cor} = Freely Corroding Surface Potential Relative to the Ag/AgCl Reference Electrode (mV)
E = Measured Surface Potential relative to the Ag/AgCl Reference Electrode (mV)
K = Constant, a Function of Tafel Slopes $[B_a B_c / 2.3(B_a + B_c)]$
R_p = Polarization Resistance, (dV/dI at $E - E_{cor} \cong 0$)
g = Specific Gravity of the Corroding Metal

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Table 1: Typical Weight Loss Values for 24 Hour Black Iron Coupon Exposure in Seattle Tap Water

Coupon	Weight Loss (mg)
1	8.5
2	10.2
3	7.8
4	7.5
5	9.3
6	6.5
7	9.3
8	6.8
9	7.2
10	8.8

Average Wt. Loss = 8.2 mg
Std. Dev. = 1.15 mg
Avg. Corrosion Rate = 200 uM/yr

Table 2: Comparison of Electrochemical Corrosion Rates with Weight Loss Measurements

	exmp 1. black iron	exmp 2. black iron	exmp 3. copper	exmp 4. galv. iron
Exposure Period	24 hrs.	7 days	7 days	7 days
Exposure Medium	Seattle tap	Seattle tap	Seattle tap	Seattle tap
Fitted Anodic Tafel Slope	250	220	80	150
Fitted Cathodic Tafel Slope	250	180	180	120
Corrosion Current Density (uA/cm^2)	10.2	7.2	1.8	1.37
Electrochemical - Corr. Rate (uM/yr.)	114	81	41	18
Average Wt. Loss (5 coupon set) (mg/day)	5.5	2.8	1.02	0.92
Weight Loss - Corr. Rate (uM/yr)	134	68	33	24
% Error - Wt. Loss vs. Electro. Corr. Rate	-15	+19	+24	-25

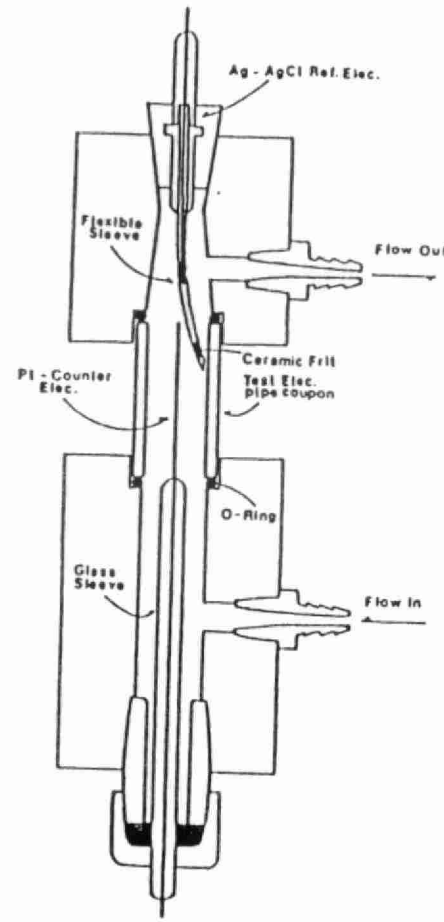


Figure 1: Cross-Section of Flo-Thru Polarization Cell

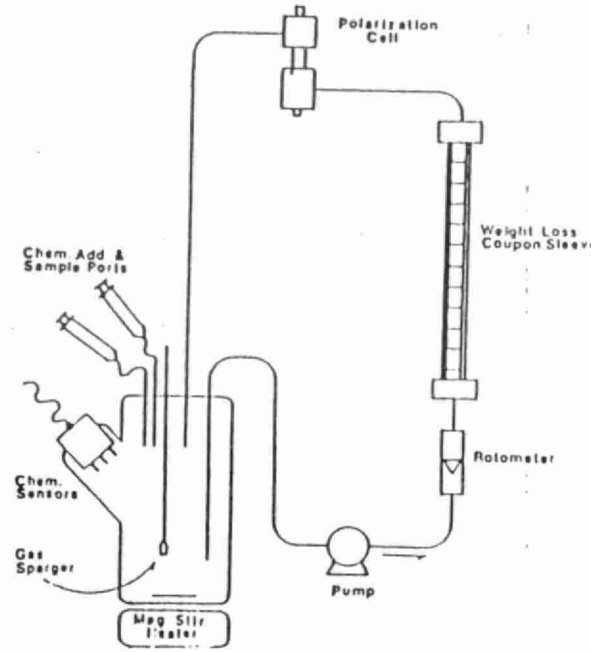


Figure 2: Schematic Diagram of Closed-Loop Recirculation System

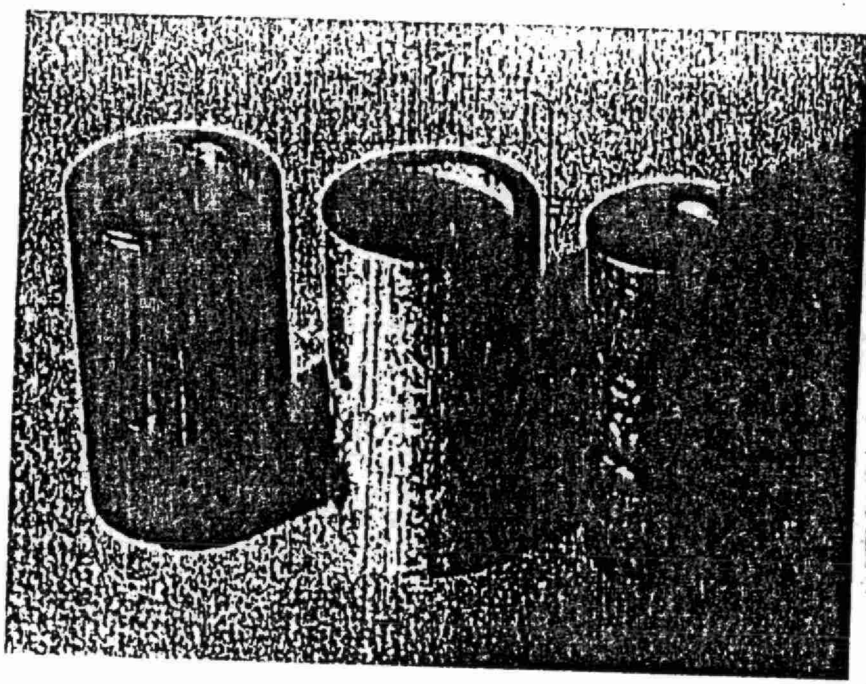


Figure 3: Typical Black Iron, Galvanized Iron and Copper Test Electrodes.

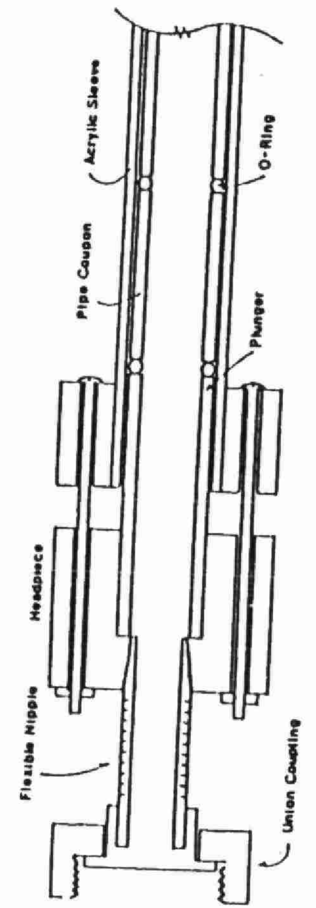


Figure 4: Cross Section of Coupon/Sleeve Assembly Used for Weight Loss Measurement

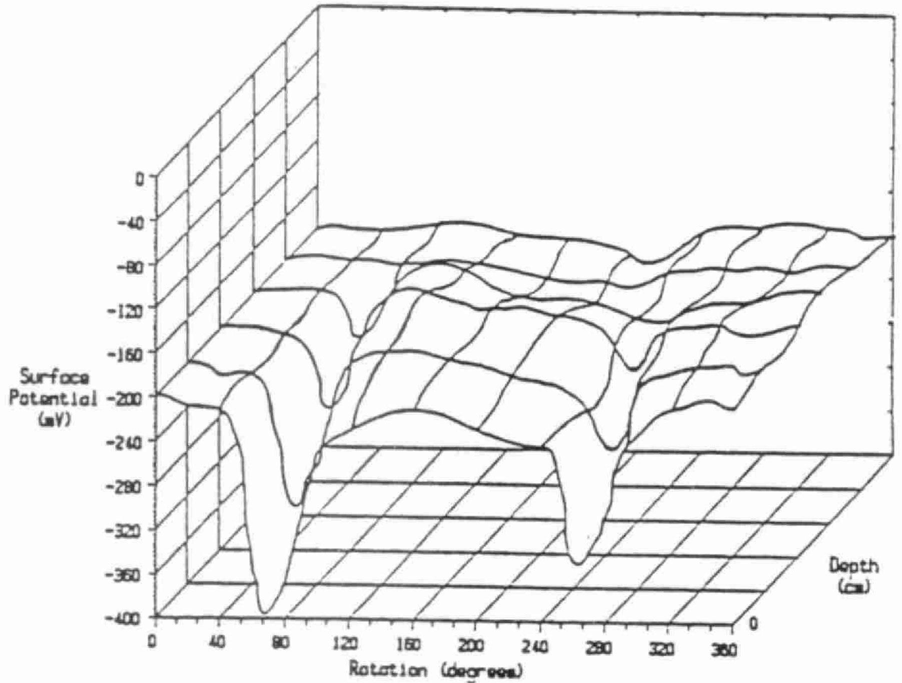


Figure 5: Surface Potential Scan Across a One-Centimeter Band of a Black Iron Electrode (96 hr. exposure)

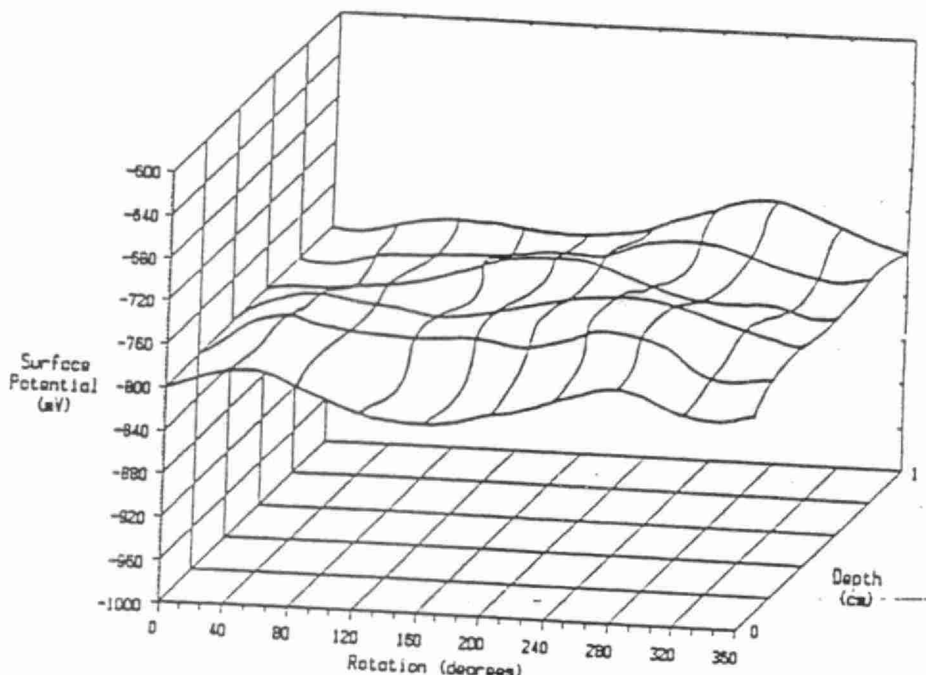


Figure 6: Surface Potential Scan Across a One-Centimeter Band of a Galvanized Iron Electrode (96 hr. exposure)

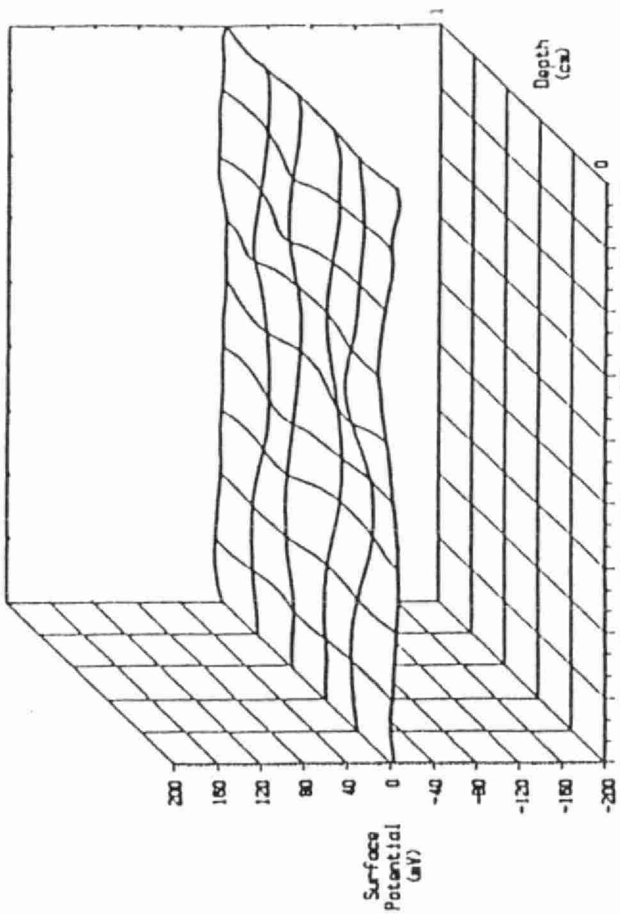


Figure 7: Surface Potential Scan Across a One-Centimeter Band of a Copper Electrode (96 hr. exposure)

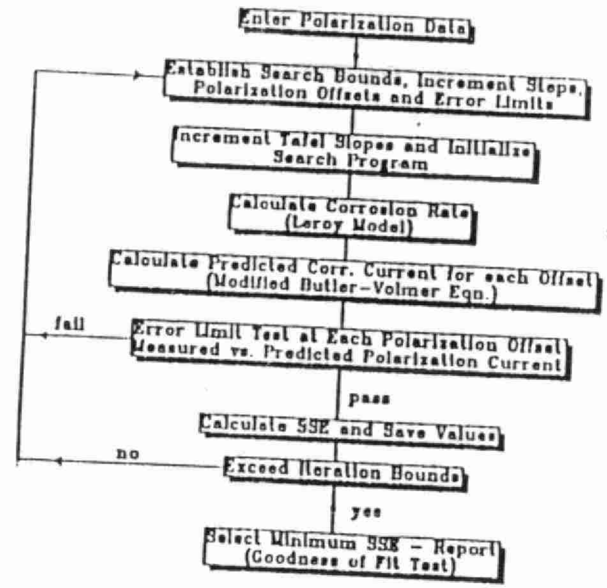


Figure 8: Flow Diagram of Tafel Slope Fitting Routine

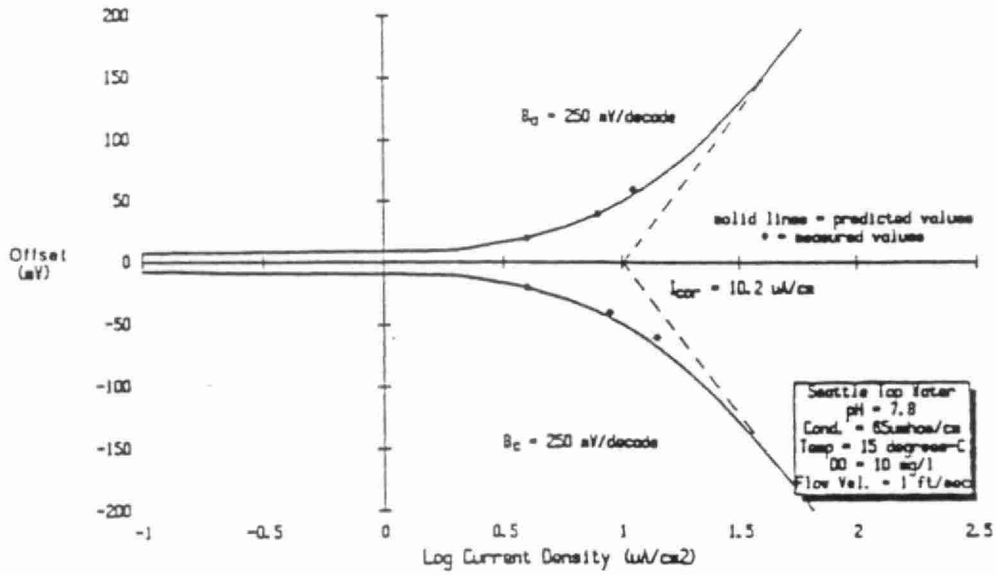


Figure 9: Evans Diagram of Measured and Predicted Polarization Currents on a Black Iron Electrode (24 hr. exposure)

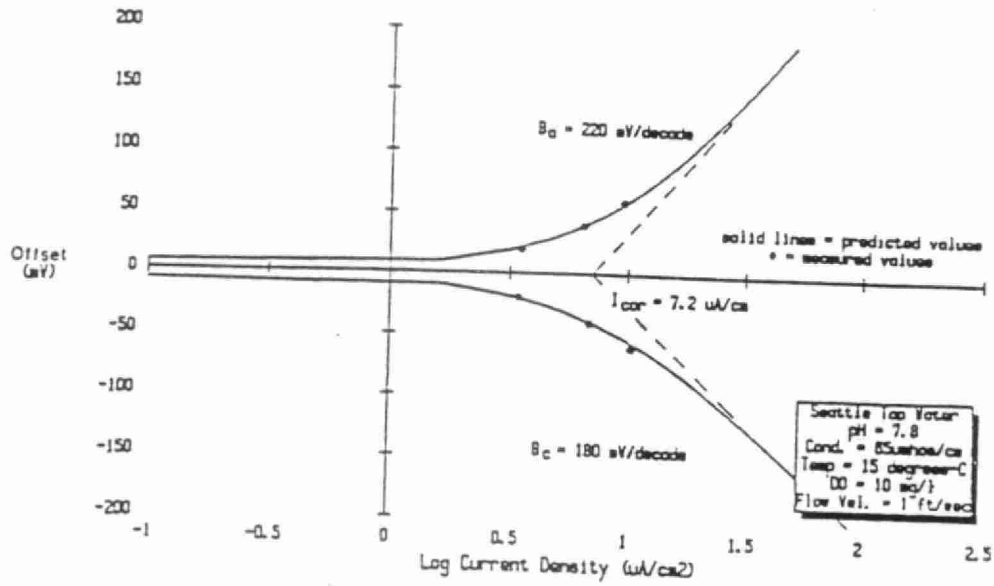


Figure 10: Evans Diagram of Measured and Predicted Polarization Currents on a Black Iron Electrode (7 day exposure)

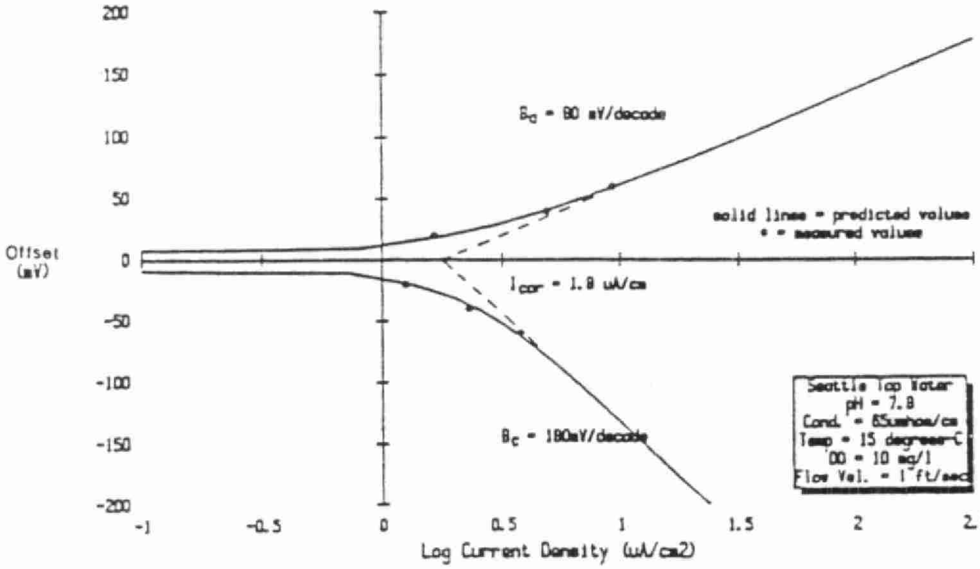


Figure 11: Evans Diagram of Measured and Predicted Polarization Currents on a Copper Electrode (7 day exposure)

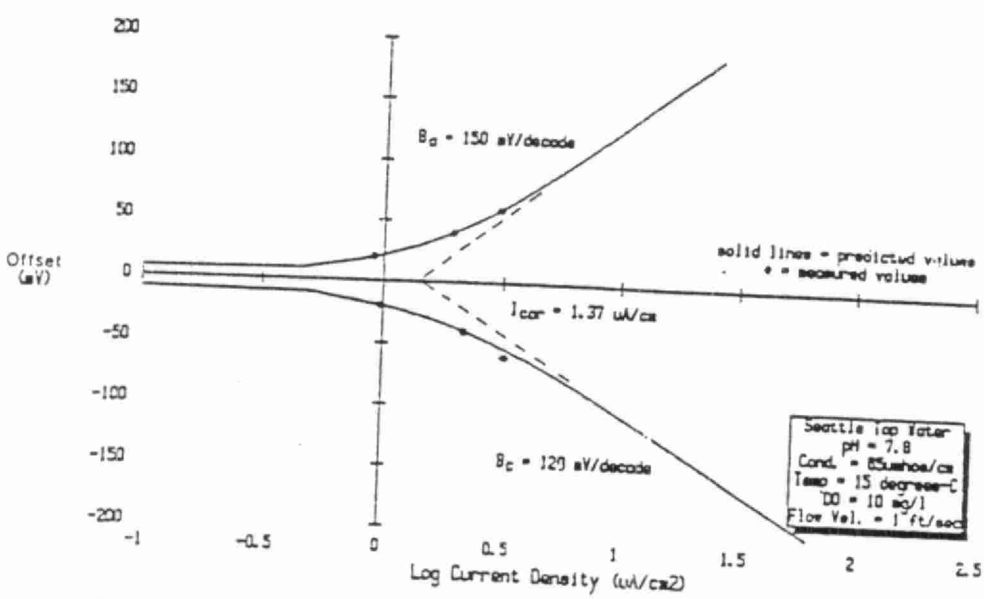


Figure 12: Evans Diagram of Measured and Predicted Polarization Currents on a Galvanized Iron Electrode (7 day exposure)

Corrosion Monitoring and Control in the Pacific Northwest

Steve H. Reiber, John F. Ferguson, and Mark M. Benjamin

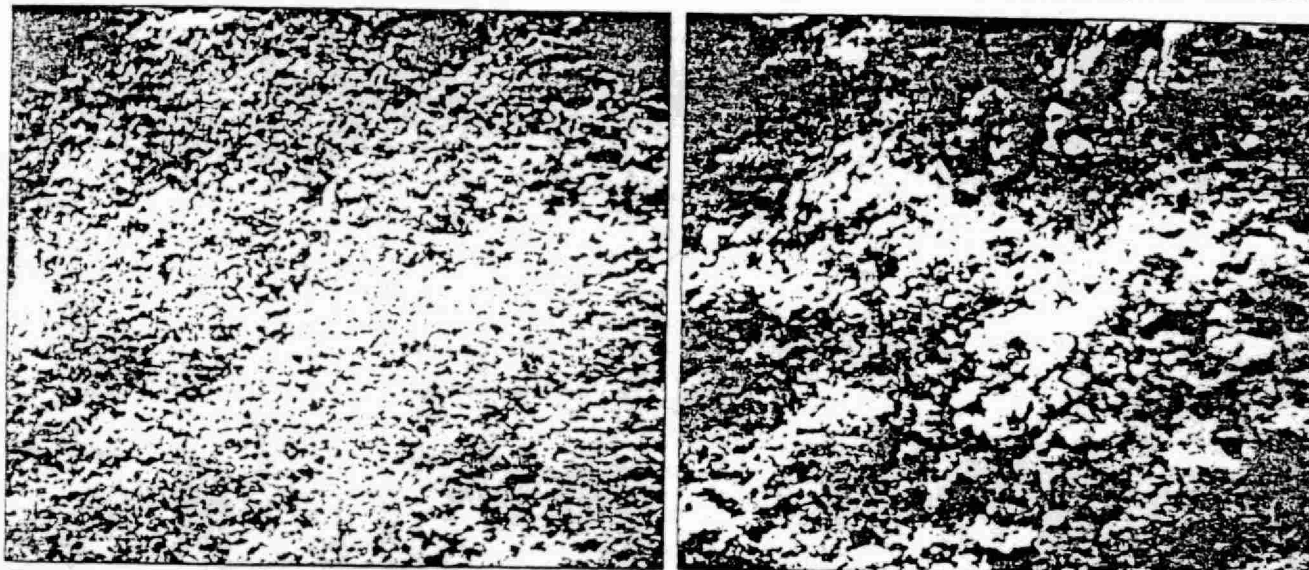
An 18-month monitoring program evaluated the relationship between copper plumbing corrosion and variations in delivered water quality in several communities in the Pacific Northwest. Significant relationships were found for copper corrosion rate dependence on pH and free chlorine residual. Regression analysis provided a statistical means of identifying the important predictors of copper corrosion rates in low mineral waters.

The northwestern United States contains some exceptionally pristine surface water sources of unusual clarity and corrosiveness. These sources, fed by mountain runoff, are often extremely low in alkalinity and pH, have negative Langelier index values, and can have substantial concentrations of leached metals, especially in tap water that has stood overnight. In 1978, the Seattle (Wash.) Water Department (SWD) estimated that the cost of replacing corrosion-damaged residential plumbing systems approached $8 million annually.[1] To reduce these costs, several northwestern communities have instituted corrosion control programs. In Seattle, a series of pilot studies[2-4] suggested that the most cost-effective technique for mitigating the problem was a program to increase pH and alkalinity through the addition of lime and soda ash.

Table 1 gives the average precorrosion and postcorrosion treatment characteristics of Seattle's Tolt River supply. Lime and soda ash feed rates during the program were 2.0 and 10.0 mg/L, respectively. The only significant changes in water quality have been in the pH and alkalinity. Other parameters such as free chlorine have not been affected.

Study objectives

The objectives of this study were threefold: (1) evaluate the success of Seattle's control program in reducing the rate of residential copper plumbing corrosion; (2) determine how instantaneous copper corrosion rates are affected by short-term variations in selected water quality parameters; (3) develop a statistical model of the copper corrosion process as a function of selected water quality parameters.



These scanning electron micrographs show the fresh (left) and aged (right) surfaces of a copper electrode at 500× magnification. The relative depth and coverage of the oxide film is readily apparent.

Materials and methods

Mobile laboratory. The US Environmental Protection Agency's Mobile Water Quality Monitoring Laboratory (MWQML) was loaned to the University of Washington for this study. The MWQML is a self-contained, microprocessor-controlled laboratory capable of continuously sampling, analyzing, and recording more than 20 water quality and corrosion-related parameters, including temperature, flow, pH, conductivity, dissolved oxygen, turbidity, total chlorine, free chlorine, fluoride, alkalinity, chloride, calcium, magnesium, copper corrosion rates, zinc corrosion rates, and particle concentrations.

The MWQML was designed, assembled, and initially tested at the National Sanitation Foundation in Ann Arbor, Mich. in 1972.[5] It was subsequently modified by The Metropolitan Water District of Southern California in 1976,[6] and by the Lawrence Berkeley Laboratory in 1980.

During this study, the MWQML was located at selected points in the Seattle distribution system for periods ranging from one to three weeks. This allowed time to develop a sufficient data base of diurnal chemical variation. Sampling was conducted for a six-month period during which the SWD increased chemical dosages to their full treatment levels and for one year after implementation of full corrosion control treatment. Sampling locations were selected to represent service lines to consumers' homes and other points of interest, such as sites near transmission lines and distribution reservoirs, rechlorination points, and transitions in service zones.

Corrosion measurement. All corrosion rate measurements were made with a three-electrode linear polarization instrument,* which was modified to accept

*Model 1000, Petrolite Instruments, Houston, Texas

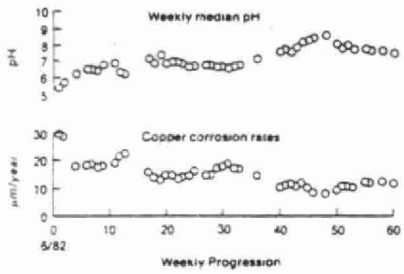


Figure 1. Average weekly aged copper corrosion rates in the Tolt distribution area during the first year of the corrosion control program

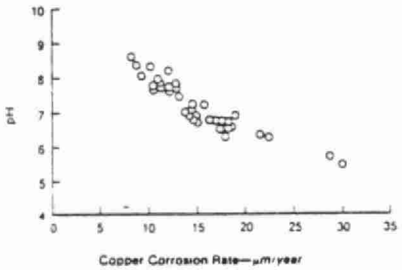


Figure 2. Copper corrosion rates (measured at selected points throughout the Seattle distribution system) as a function of weekly median pH

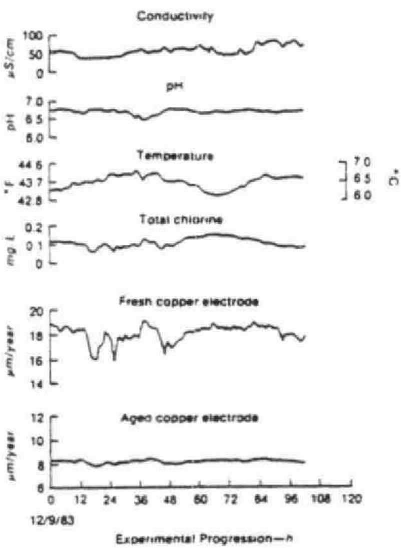


Figure 3. Continuous copper corrosion rates on fresh and aged electrodes compared with selected water quality parameters

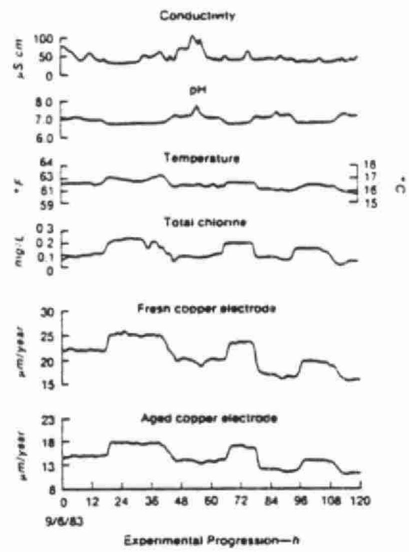


Figure 4. Continuous copper corrosion rates on fresh and aged electrodes compared with selected water quality parameters

TABLE 1

Water quality in the northern Seattle distribution area

Parameter	Delivered Water Quality	
	Precorrosion Treatment	Postcorrosion Treatment
pH	5.7-6.2	7.8-8.3
Alkalinity—*mg as* $CaCO_3$*/L*	3.0-5.0	15.0-17.0
Conductivity—*μmhos/cm*	30.0-40.0	50.0-75.0
Free chlorine residual—*mg/L*	0.2-0.4	0.2-0.4

TABLE 2

Linear regression models of copper corrosion on aged and fresh surfaces

Parameter	Coefficient	
	Aged Surface	Fresh Surface
Corrosion Rate		
Y intercept	14.04	46.22
pH	-1.98	-2.31
Free chlorine residual—*mg/L*	20.57	33.53
Temperature—°*F* (°*C*)	33.1 (0.66)	32.5 (0.33)
Conductivity—*μmhos/cm*	0.01	0.02

sequencing and data acquisition control by the MWQML microprocessor. The system measures a corrosion rate by polarizing (i.e., shifting the potential at) the test electrode in a technique first described by Stern and Geary.[7] For very small changes in potential, the corrosion rate under freely corroding conditions is proportional to the impressed current needed to maintain the polarization shift. In effect, the instrument consists of a potentiostat and an extremely sensitive ammeter capable of measuring currents in the microampere range.

The corrosion electrodes were positioned in flow-through cells with a constant-head device to ensure stable liquid velocities. The electrodes used were standard cylindrical probes, 99.9 percent pure copper with a total surface area of 18 sq cm. Cycle times allowed individual corrosion measurements to be taken at 10-min intervals.

A multiplexer attached to the monitor made it possible to automatically sequence corrosion rate measurements on two sets of electrodes. Copper plumbing materials with different degrees of corrosion were represented by two electrode sets with different oxide film depths. The first set, an "aged" copper surface, was covered with a stable oxide film layer more than 50 μm deep. The coating developed over a period of eight months and was both uniform and continuous. The second electrode set represented a relatively "fresh" copper surface, with a shallow oxide film layer approximately 10-20 μm deep.

Although a heavy oxide film layer was left intact on the aged surface, significant oxide buildup on the fresh surface was prevented through a program of regularly scheduled weekly washings using a nonabrasive detergent paste. The paste was applied manually with cotton swabs, using gentle pressure. Washing reduced the extent of oxide buildup but did not expose a clean or bare copper surface. An entirely bare surface would require a substantial conditioning period because initial corrosion rates would be high and would constantly decline as the oxide layer developed.

Both optical and scanning electron microscopic examination of the corroding electrode surfaces confirmed that uniform copper corrosion was the prevalent form within the Seattle system. No examples of cold water pitting were observed. Because the corrosion was uniform, corrosion rates are presented as a penetration velocity in microns per year (1 μm/year = 0.039 mils per year [mpy]).

The MWQML corrosion rate meter was evaluated by comparing its results with weight-loss measurements of the fresh copper electrode set. Weekly weight-loss comparisons of the three individual electrodes with the cumulative average linear polarization measurement for the same period showed that the MWQML meter consistently gave a corrosion rate reading 25 percent lower than the weight-loss measurement. Given the inaccuracies and variability in both types of measurements, this was considered a satisfactory validation of the linear polarization technique.

The Seattle program

Seattle began its program of corrosion control in June 1982. The program called for the gradual increase of distribution

water pH and alkalinity through the addition of lime and soda ash. The adjustment period extended over 12 months, beginning in June 1982. During startup, corrosion rates were followed on aged copper electrodes at selected sites throughout the northern portion of the distribution area. Corrosion rates on fresh copper surfaces were not available during this period. Figure 1 summarizes the weekly median pH values and the aged copper corrosion rates that were obtained during this first year of operation. The data clearly indicate that as the pH of the system was adjusted upward, there was a reciprocal decrease in the copper corrosion rate. Overall, the pH shifted from a median distribution level of approximately 5.8 at the start of the program to a median level of 7.7 after 12 months of operation, producing a decrease in corrosion rates from a weekly average of 21.6 μm/year to 10.2 μm/year (a 54 percent decline).

Figure 2 shows the weekly median aged copper corrosion values of Figure 1, plotted as a function of the median pH. The inverse relationship between pH and distribution copper corrosion is clear and has been observed by other researchers. Hilburn[8] has postulated that copper corrosion rates may be limited by the transport of hydroxyl ions away from the corroding surface. The hydroxyl ions are formed in the oxygen half-cell reduction:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

Their increase at the point of corrosion produces a higher localized pH on the copper surface than in the bulk fluid. Increased hydroxyl ion concentrations diminish the cathodic half-cell reaction rate, thus inhibiting the overall rate of corrosion. By increasing the pH of the bulk solution, the driving force for diffusional transport of the hydroxyl ions away from the copper surface is decreased.

It is also known that a higher pH decreases the solubility of copper oxide solids, enhancing the buildup of an oxide film layer over time. This increases the diffusional barrier further, reducing the overall corrosion rate.

As part of its corrosion control program, SWD conducted a study of metal plumbing leaching rates in 300 Seattle residences.[9] Homes were selected from the entire service area, and sample collection was concentrated primarily on water that had stood overnight. For homes in the northern distribution area, study results after the first 12 months of treatment indicate that concentrations of cadmium, lead, and copper were reduced by 48, 12, and 60 percent, respectively. Although these results are not directly comparable with the electrochemically measured reduction in copper corrosion, both studies indicated that the corrosion control program is successful.

Copper corrosion and short-term water quality variation

Once water is delivered to the distribution system, its quality can be influenced by rechlorination, storage in open reservoirs, piping systems, and other factors. Water delivered to a specific connection may be a blend from several storage facilities. The relative proportions of the blend would depend on system demand and network hydraulics. Diurnal variations over a range of as much as 1.0 pH unit and 0.6 mg chlorine/L are common in some portions of Seattle's distribution system. Temperature may vary by several degrees. Less significant variations in conductivity are observed. Variation in alkalinity is minor and directly related to the pH variation. Hardness variation is insignificant and generally below the sensitivity of the standard titration. Dissolved oxygen levels remain nearly constant, close to saturation levels.

Monitoring for short-term water quality variations and their impact on copper corrosion rates was conducted at numerous points throughout the northern Seattle distribution network. Figures 3 and 4 are summaries of water quality variations and copper corrosion rates on both fresh and aged copper surfaces at two different sampling points during a five-day sampling period. To present the full five days of data, hourly averages are shown. Each hourly value is the average of six 10-min incremental values. The standard deviations of the hourly and 10-min data sets are nearly identical, indicating that little of the quality of variation in the data was lost by the hourly averaging.

Both Figures 3 and 4 demonstrate a strong positive correlation of corrosion rate with free chlorine residual for the fresh copper surfaces. Corrosion rates on the aged surfaces are substantially less than the fresh surfaces because of the protection provided by the thicker oxide film. The relationship between the aged surface corrosion rate and the chlorine concentration in Figure 4 is weak compared with the data set in Figure 3, probably as a result of the lesser magnitude of free chlorine variation and its more gradual rate of change. Variation of the aged copper corrosion rate, however, follows a similar pattern to that of the fresh surface, indicating that the same fundamental mechanisms are at work on both.

The influence of pH on the copper corrosion rate is equally apparent in Figure 3. A distinct inverse relationship of the corrosion rate with pH change exists, including the more pronounced pH spikes. For this data set, pH and chlorine residual were roughly equal in their correlation to the copper corrosion rate. Of course, they are strongly correlated with each other as well. For the data set in Figure 4, pH was somewhat less correlated to the copper corrosion rate. The influence of temperature and conductivity are not readily apparent in either data set.

Statistical analysis

Multiple linear regression analysis was performed on a combination of selected data sets to evaluate the relative significance of the four water quality parameters on both fresh and aged copper surface corrosion rates. The combined data set spanned more than 500 h and contained more than 4000 individual data points, including the data shown in Figures 3 and 4. A forward stepwise regression analysis was used, with the four independent predictor values regressed in the following sequence: (1) pH, (2) free chlorine residual, (3) temperature, and (4) conductivity. Table 2 presents the linear regression models developed for both the fresh and aged copper surfaces.

Table 3 presents the regression analysis of variance for the aged and fresh surface corrosion rates. The coefficient of determination (R^2) indicates that the regression models account for approximately 96 and 76 percent, respectively, of the overall variance. The overall regression for both equations is significant at the 99 percent confidence level. The sum of the squares analysis on the four independent regression parameters indicates that for both aged and fresh surfaces, the free chlorine residual is the most significant predictor value—accounting for more than 60 percent of the variance in the corrosion rates. On the aged surface, the significance of the pH and temperature predictors is approximately equal, accounting for about 15 percent of the observed variance. Both parameters are of less significance on the fresh surface. Conductivity is of little significance as a predictor value for either the fresh or aged surfaces in the Seattle distribution network.

The predominance of chlorine in the regression analysis was quite unexpected, given the emphasis on pH control to reduce corrosion rates and the very strong correlation with pH observed in some data sets (e.g., Figure 3). The model results are, however, unambiguous. The regression equation coefficients indicate that the corrosion rate change with chlorine residual is approximately +25.0 μm/year per mg chlorine/L, whereas the change with pH is approximately −2.5 μm/year per pH unit, a value somewhat smaller than that indicated by the results presented in Figure 3. In addition, the chlorine residual accounted for 60–90 percent of the

TABLE 3

Analysis of variance for aged and fresh copper surface corrosion regression models

Cause of Variance	Degrees of Freedom	Sequential Sum of Squares		Coefficient of Determination—R^2	
		Aged	Fresh	Aged	Fresh
Residual	346	0.118	0.373		
Regression	4	2.238	1.170	0.950	0.758
pH	1	0.354	0.001	0.15	0.001
Free chlorine	1	1.491	1.055	0.632	0.684
Temperature	1	0.385	0.076	0.163	0.050
Conductivity	1	0.008	0.036	0.003	0.023
Total*	350	2.356	1.541		

*Excluding regression

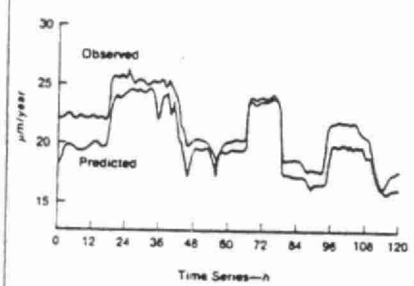


Figure 5. Observed versus predicted copper corrosion rates on a fresh electrode surface

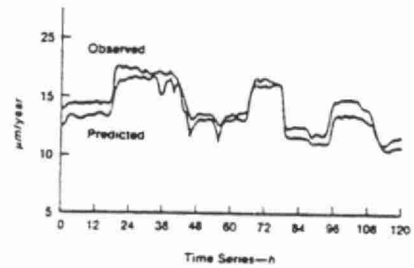


Figure 6. Observed versus predicted copper corrosion rates on an aged electrode surface

observed coefficient of determination, whereas the pH accounted for 16 percent of the aged surface values and less than 1 percent of the fresh surface values.

The greater influence of pH on aged surface corrosion is probably related to the boundary layer created by the oxide film. By diminishing contact of the bulk fluid with the metal surface, the film creates a diffusional limitation for the hydroxyl ions that are generated in the oxygen reduction half reaction at the copper surface. The film also acts as a diffusional barrier to the free chlorine in solution and therefore diminishes the impact of this parameter on the overall corrosion rate.

Whereas the thin film of the fresh copper surface does not allow a significant difference between bulk solution and surface pH, the thick film of the aged electrode retards the diffusion of hydroxyl ions away from the surface and creates a surface pH high enough to decrease the velocity of the oxygen half-cell reaction. Because of the diminished effect of the chlorine and the probable importance of the surface pH on the aged electrode, the bulk fluid pH becomes important in determining the driving force for the transport of hydroxyl ions across "thick" films and thus shows a stronger relationship to the overall corrosion rate.

Figures 5 and 6 present comparisons of the statistical model predictions of copper corrosion rates on fresh and aged surfaces with the observed corrosion rates. The data set used for comparison is the same one presented in Figure 3. Values of R^2 for these subset comparisons are 0.72 and 0.81 respectively, indicating a good fit.

Conclusions

The Seattle water system is unusual because of its extremely high quality water sources and the minimal treatment provided these sources. In evaluating the results of this study, the character of Seattle's water sources—namely, their unusually low alkalinity and buffer capacity and their extremely low mineral content—must be kept in mind. Extrapolation from the Seattle corrosion experience to water sources of higher mineral content may be unsuccessful because of competing chemical equilibriums. The major conclusions that can be drawn from this study are summarized below.

- Seattle's program of corrosion control through pH adjustment and alkalinity addition has been successful in reducing the overall rate of corrosion on aged copper surfaces.
- Variation in corrosion rates can be successfully evaluated as a function of short-term changes in water quality conditions. Regression analysis of these variations can produce linear models that accurately predict corrosion rates.
- The oxide film layer on the aged copper surface provides substantial protection. Compared with the relatively clean surfaces of new copper plumbing, the oxide film of an aged surface reduces the corrosion rate by about 50 percent.
- Of the four parameters tested, the free chlorine residual is the most important in predicting copper corrosion rates. On both relatively fresh and aged surfaces, the variations in chlorine residual accounted for more than 50 percent of the overall variation in copper corrosion rate.
- On the waters tested, pH is a predictor of little importance for corrosion on relatively clean copper surfaces, but it is of value on surfaces with a heavy oxide layer. This may indicate that the creation of a hydroxyl ion transport limited condition is facilitated by the presence of an oxide film.
- Conductivity appears to be of little importance as a predictor of copper corrosion rates in low alkalinity waters.

Acknowledgment

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The Effects of Short-Term Changes in Water Quality on Copper and Zinc Corrosion Rates

Al Stone, Dimitris Spyridakis, Mark Benjamin, John Ferguson, Steve Reiber, and Stein Osterhus

In this study, the linear polarization technique was used to evaluate changes in the corrosion rates of copper and zinc surfaces in response to short-term changes in water quality. This analytical technique can be applied wherever uniform corrosion, as opposed to pitting, is occurring. The parameters investigated included temperature, pH, dissolved oxygen, chlorine residual, flow, and conductivity. All the parameters except flow rate affected copper corrosion rates. Conductivity, dissolved oxygen, chlorine residual, and temperature affected zinc corrosion rates. Reproducible corrosion rates were obtained within a few minutes of the changes in water quality.

Over at least the past 10 years, the city of Seattle, Wash., has been faced with the problem of significant corrosion of household plumbing. A relatively high incidence of pipe failures and consumer complaints of colored water led the Seattle Water Department, in 1975, to initiate a study of the causes of the corrosion and potential mitigating strategies.[1]

Seattle obtains its water from two sources, the Tolt and Cedar rivers, both of which have their headwaters near the crest of the Cascade mountain range. Although the water from both sources is very pure, the study indicated that the water, particularly from the Tolt, was quite corrosive, as a result of low values of pH (6.5–7.0) and alkalinity (10–15 mg as $CaCO_3$/L). After chlorination and fluoridation, the pH declined to as low as 6.0 and the alkalinity to <5 mg as $CaCO_3$/L.

Exposure of metal coupons to the distribution system water confirmed that the rates of corrosion for copper, zinc, lead, and iron were excessive, and a corrosion control program was implemented whereby lime and soda ash were added to increase the pH and alkalinity of water in the distribution system. Beginning in summer 1982, the US Environmental Protection Agency (USEPA) funded an additional study to evaluate the effects of the chemical addition on the water quality and corrosion rates. One objective of that study, the results of which are presented here, was to evaluate the relative importance of several water quality parameters in the corrosion of fresh and aged copper and aged zinc (galvanized iron) surfaces in low alkalinity waters.

Theoretical considerations

Corrosion. Corrosion is an electrochemical process in which metal is oxidized and an electron acceptor (usually oxygen [O_2] or hydronium ion [H^+]) is reduced:

Oxidation: $Me^0 = Me^{n+} + ne^-$

Reduction of O_2: $O_2 + 4H^+ + 4e^- = 2H_2O$

Reduction of H^+: $2H^+ + 2e^- = H_2$

After removal from the corrosion rate monitor, these electrodes showed the effects of aging and film growth.

If a chlorine (Cl) residual is present, it may also act as an electron acceptor:

$$HOCl + H^+ + 2e^- = Cl^- + H_2O$$

The corrosion process sometimes leads to the deposition of an oxidized film on the surface of the corroding metal. In the cases of zinc and copper, oxides, hydroxides, carbonates, and hydroxycarbonates of the corroding metals can be deposited. These films can slow corrosion by protecting the underlying layers from contact with the corroding medium.

As in all chemical reactions, the net rate of each of these reactions is determined by the relative rates of a forward and reverse reaction. Electrochemical reactions are unique in that the forward and reverse half-reactions often take place at sites that are separated spatially. The reactions are linked by the transfer of electrons through the metal. Because the reactions involve the transfer of electrons, their rates are dependent on the electrochemical potential of the system. The relationship between the electrochemical potential and the rates at which electrons are released (at the anode) or consumed (at the cathode) is described by the Butler–Volmer equation:

$$i = i^0 \left\{ \exp[(1-\beta) F\eta / RT] - \exp[-\beta F\eta / RT] \right\}$$

in which η = overpotential $E-E^0$; E = electrochemical potential at the electrode; E^0 = equilibrium potential, i.e., the potential at which the thermodynamic driving force for the reaction is zero; i = exchange current density, i.e., the electrical current flowing per unit area of electrode; i^0 = equilibrium exchange current density, i.e., the value of i when $E = E^0$;* F = Faraday constant; R = gas law constant; T = absolute temperature; and β = symmetry factor, a constant characteristic of the system.

Two equations such as the one above are applicable in each system—one at the anode and one at the cathode. For fixed solution conditions, there is a unique value of E such that electrons are released by the anodic reaction and consumed by the cathodic reaction at equal rates, and toward which the system will tend. This value of E is designated the corrosion potential, E_{corr}; the corresponding current density is designated i_{corr} and is called the corrosion current.

At potentials E such that $\eta \geq 100$ mV, one of the exponential terms in the Butler–Volmer equation is negligible and the equation reduces to

$$\log i = \log i^0 + \left\{ [(A-\beta) F] / (2.303 RT) \right\} (\eta)$$

in which $A = 0$ or 1, depending on which term is negligible. The proportionality constant relating η and $\log i$ is called the Tafel slope and is characteristic of the system.

Linear polarization. The process used to

*When $E = E^0$, the rates of the oxidation and reduction reactions are equal, so no net reaction occurs; i^0 is the gross rate of oxidation (or reduction) under these conditions and is non-zero.

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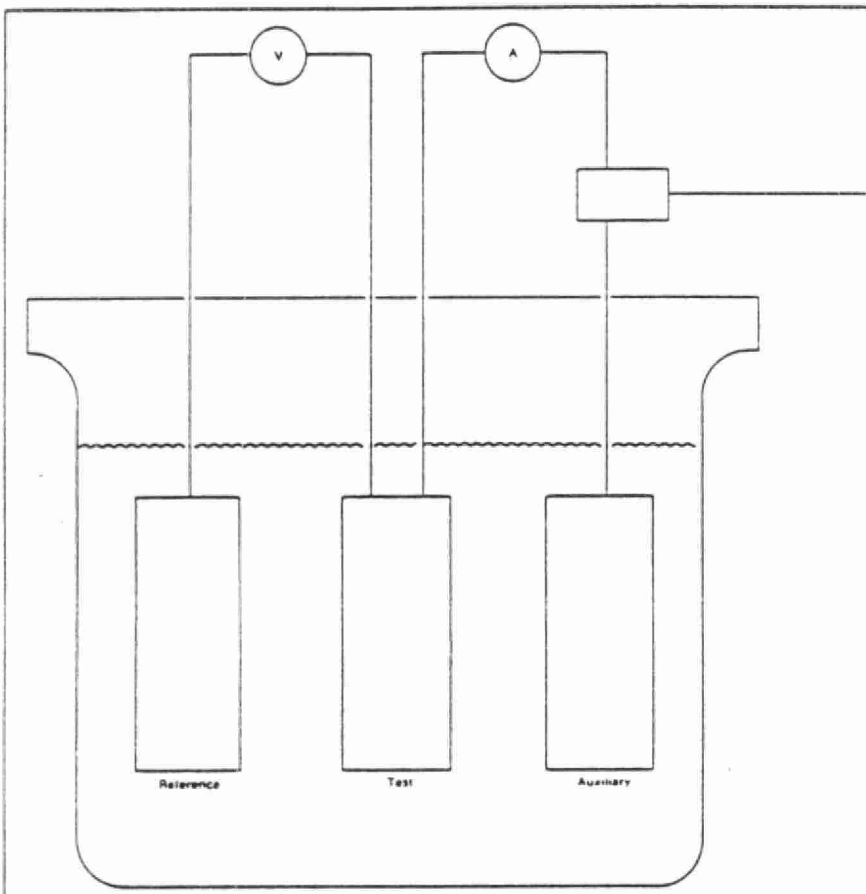

Figure 1. Configuration of the three-electrode system used in the corrosion rate monitor

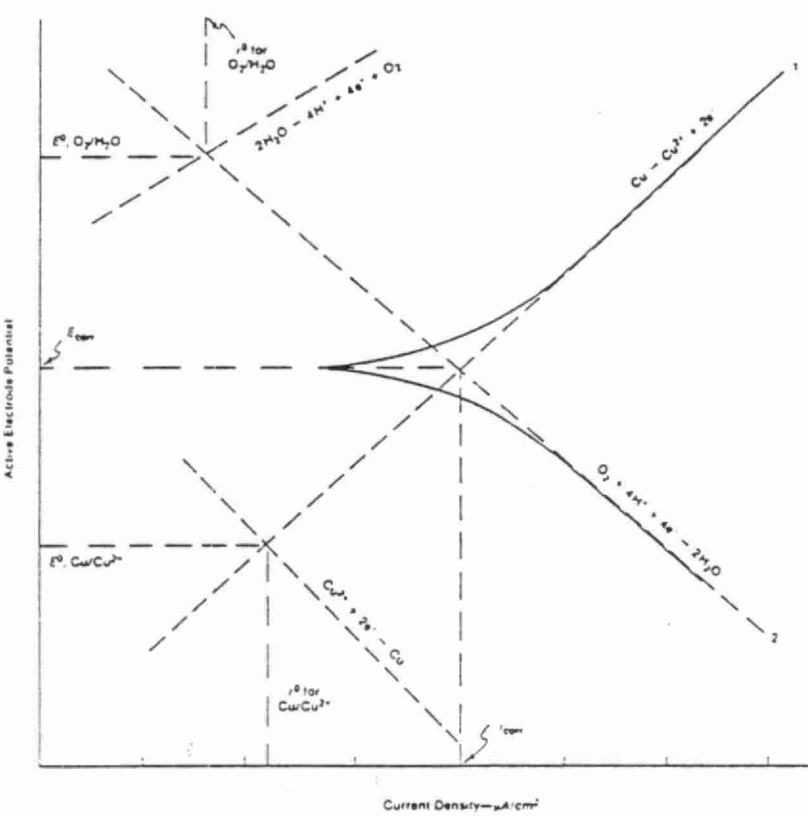

Figure 2. Potential versus current responses for the copper–oxygen system *(1—anodic oxidation curve; 2—cathodic reduction curve)*

determine corrosion rates in this work, the linear polarization technique, was first developed by Stern and Geary.[2] The apparatus used involves a system of three electrodes, all made of the metal of interest (Figure 1). The reference electrode is used to zero the system before the corrosion rate is determined. The remaining two electrodes, the auxiliary and the test electrode, provide the anodic and cathodic sites for the corrosion reaction. When the electrodes are initially exposed to the solution, their potentials should move toward the corrosion potential. Each electrode will have anodic and cathodic sites and will corrode at a rate given by i_{corr}; however, this current, the quantity of interest, is not directly measurable. When a small potential difference is imposed between the test and auxiliary electrodes, one becomes primarily anodic and the other primarily cathodic, and a measurable current flows between them. If the applied voltage is sufficiently small, this current can be related to the corrosion current by

$$\Delta E/\Delta i = (1/2.303\, i_{corr}) [(B_a B_c)/(B_a + B_c)]$$

in which ΔE = applied change in potential, Δi = change in current density resulting from the applied potential, B_a = anodic Tafel slope, and B_c = cathodic Tafel slope.

In reality, nonhomogeneities in the electrodes may cause a small potential difference to develop between the electrodes and, hence, a small current to flow, even in the absence of an externally applied potential. This current is sensed and compensated for during the subsequent measurement. If a known ΔE is applied and it is assumed that the values for the Tafel slopes are constant, the above equation can be reduced to

$$\Delta i = (K)(i_{corr})$$

in which K is a known constant. Thus the corrosion current can be obtained by measuring Δi.

Typical potential versus current responses are shown for anodic and cathodic half-reactions in Figure 2, which also shows the corrosion potential and current for the overall corrosion reaction.

This discussion and the derivation of Stern and Geary are based on the assumption that uniform corrosion is taking place. The technique is well suited for copper and zinc, the metals chosen for this study, which often exhibit uniform corrosion in low alkalinity, aggressive waters such as found in Seattle. By contrast, iron and steel surfaces typically corrode nonuniformly, forming pits overgrown by tubercles of corrosion products. Linear polarization corrosion rates in these latter cases are complex functions of system geometry and must be interpreted on a case-by-case basis.

Materials and methods

Equipment. The equipment used in these experiments was housed in the USEPA Mobile Water Quality Monitoring Laboratory. Table 1 lists the parameters measured and the instrumentation employed in each analysis. Calibration of the chemical instruments followed manufacturers' recommendations and procedures in *Standard Methods*.[3] The laboratory contains an on-line data acquisition system which takes a reading from each experimental instrument every 10 min and then stores the data on a disk.

Corrosion rates were measured using a corrosion rate monitor (CRM),* which includes three sets of electrodes. During a data acquisition cycle, the system cycles to a new set of electrodes, allowing 30 s for equilibration, followed by 90 s during which the corrosion rate is determined. At the end of the 2-min cycle, the results are stored and the CRM accesses the next electrode assembly. Since corrosion rates were monitored for both anodic and cathodic ΔEs using three sets of electrodes, a total of six rates were measured, with each rate being measured once every 12 min.

The three metal surfaces chosen for the study were fresh copper (Cu), aged Cu, and aged zinc (Zn). The aged Cu and aged Zn electrodes were allowed to corrode in ambient Seattle tap water over several months. Copper and zinc oxide films accumulated on the aged electrodes. The thicknesses of the continuous films were approximately 50 μm and 1 mm (2 and 39 mils) for the Cu and Zn electrodes, respectively. The response of the corrosion rates of these electrodes to changes in water quality is presumably similar, at least in a qualitative sense, to that of older home plumbing systems.

Fresh Cu electrodes were used in a third cell. These electrodes were removed from the cell, and much of the accumulated film was removed with a nonabrasive cleanser and cotton swabs before each data set was collected. In this way, the corrosion rates in the presence and absence of the long-term growth of oxidized Cu film could be compared. The rates of response of the two copper systems to water quality changes were also compared.

During normal operation, the water flows in a single pass through the laboratory instruments and then is wasted. For these tests, the flow system was altered to provide for recycling in order to maintain constant water quality conditions. Water of the desired composition was stored in a 55-gal (210-L) reservoir (Figure 3) and was fed directly into the monitoring system. The effluent from the instrumentation cells was collected and returned to the storage tank, from which it was recycled throughout the experiment.

TABLE 1

Parameters measured and equipment used

Parameter	Unit of Measurement	Instrument Used
Temperature	°C	Model R 25 Robot Monitor,* Schneider Instruments Inc., Cincinnati, Ohio
Flow	gpm	CE in-line flowmeter, In-Val-Co, Tulsa, Okla.
pH		Combination electrode: part of Robot Monitor,* Schneider Instruments Inc., Cincinnati, Ohio
Conductivity	μS/cm	Conductivity probe: part of Robot Monitor,* Schneider Instruments Inc., Cincinnati, Ohio
Turbidity	ntu	Model A80-1-1-2-0 turbidimeter, Great Lakes Instrument Co., Milwaukee, Wis.
Dissolved oxygen	mg/L	Model 8000 dissolved oxygen probe, L.G. Nester Inc., Millville, N.J.
Total chlorine residual	mg as Cl/L	Model 872 chlorine residual monitor, Capital Controls Co., Colmar, Pa.
Free chlorine residual	mg as Cl/L	Model 871 chlorine residual monitor, Capital Controls Co., Colmar, Pa.
Corrosion rate	mils/year	Model M1000 corrosion rate monitor, Petrolite Inc., Houston, Texas

*Robot Monitor Automatic Water Quality Analysis System

TABLE 2

Baseline values used in experiments

Parameter	Value
Temperature	59°F (15°C)
pH	7.0
Conductivity	100 μS/cm
Turbidity	uncontrolled, <2 ntu
Dissolved oxygen	saturation
Chlorine residual	0 mg/L
Flow velocity	5.6 cm/s

TABLE 3

Reproducibility of linear polarization results for replicate measurements made under three water quality conditions

Parameter	Test 1	Test 2	Test 3
Temperature—*°C*	11.4 ± 0.4	12.6 ± 1.1	15.5 ± 3
Flow—*cm/s*	5.6 ± 0.4	5.5 ± 0.5	5.5 ± 0.2
pH	7.0 ± 0.1	6.6 ± 0.6	6.7 ± 0.5
Conductivity—*μS/cm*	167.0 ± 13	90.8 ± 2.2	6.2 ± 0.5
Turbidity—*ntu*	1.4 ± 0.3	0.6 ± 0.5	0.8 ± 0.7
Dissolved oxygen—*mg/L*	12.3 ± 1.4	9.1 ± 0.5	11.1 ± 2.1
Total chlorine residual—*mg as Cl/L*	0	0	0
Corrosion rate—*μm/year*			
Fresh copper	1.14 ± 0.17 (15 percent)	0.67 ± 0.13 (19 percent)	0.33 ± 0.05 (15 percent)
Aged copper	0.41 ± .07 (17 percent)	0.34 ± 0.04 (12 percent)	0.20 ± 0.03 (13 percent)
Aged zinc	0.96 ± 0.36 (37 percent)	0.53 ± 0.21 (39 percent)	0.24 ± 0.03 (13 percent)

The parameters studied were dissolved O_2, Cl residual, pH, flow rate, temperature, and conductivity. These parameters were chosen because they are expected to influence corrosion rate and because some are affected by water treatment, thereby influencing corrosion rate. Chlorine residual was adjusted with a sodium hypochlorite solution and was all in the free Cl form. The pH was adjusted using sodium hydroxide or hydrochloric acid. Conductivity was adjusted using sodium chloride, sodium sulfate, or sodium bicarbonate.

Tap water was used in all experiments except for those evaluating the effect of conductivity, for which it was necessary to use glass-distilled water to study the extreme low conductivity range. Twenty millilitres of a saturated sodium sulfite solution was added to each batch of tap water to assure complete reduction of any Cl residual.

Experiments usually started with fresh water, and the parameter of interest was adjusted by adding appropriate chemicals. For all cases except conductivity, data from several days and several runs were combined for analysis. Insofar as possible, parameter changes were made so that increases and decreases in parameter value alternated during a series of tests.

Concentrated stock solutions were prepared with reagent-grade chemicals. Once data were obtained for a particular

*Model 1000 series, Petrolite Inc., Houston, Texas

water quality, an aliquot of the stock solution was added to change the parameter of interest. All other parameters were maintained near baseline (Table 2). When necessary and feasible, additional chemicals were used to maintain baseline conditions.

It was not always feasible to vary only one test parameter at a time. The addition of some chemicals caused not only the parameter of interest to change but caused other baseline values to vary as well. For example, when conductivity was varied, the addition of sodium bicarbonate caused the pH to increase. In other tests, temperature slowly changed toward the ambient value. In these instances, the laboratory monitoring system was used to track the water quality parameters of interest. The data were then evaluated statistically to determine the relative effects of variation of incidental parameters on the corrosion rate. In all cases the effect of the experimental parameter predominated over the effects of the variation in another parameter, such as temperature or pH drift. Thus, the data are presented without correction for such drift.

Corrosion measurements were not recorded until stable readings were attained, i.e., until the rates remained constant for three consecutive readings (36 min). Once readings were begun, a test lasted 1-2 h. Overall, a series of tests to study the effects of a single water quality parameter was completed in less than 3 h.

Reproducibility of measurements. At least five replicate tests were conducted at three different baseline conditions to determine the reproducibility of the corrosion data. The results were acceptably reproducible under each set of conditions (Table 3). The Zn system was much more susceptible than the Cu systems to random fluctuations, with the relative standard deviation in measured corrosion rate being slightly less than 40 percent. For both copper systems, the relative standard deviation was <20 percent, a value similar to that obtained in coupon tests with Seattle tap water.

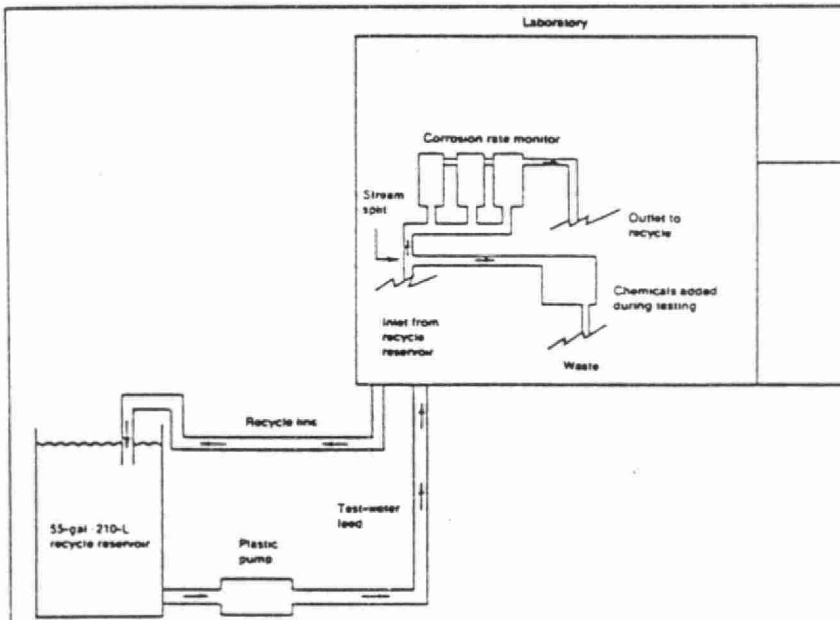

Figure 3. Configuration of test equipment added to the Mobile Water Quality Monitoring Laboratory

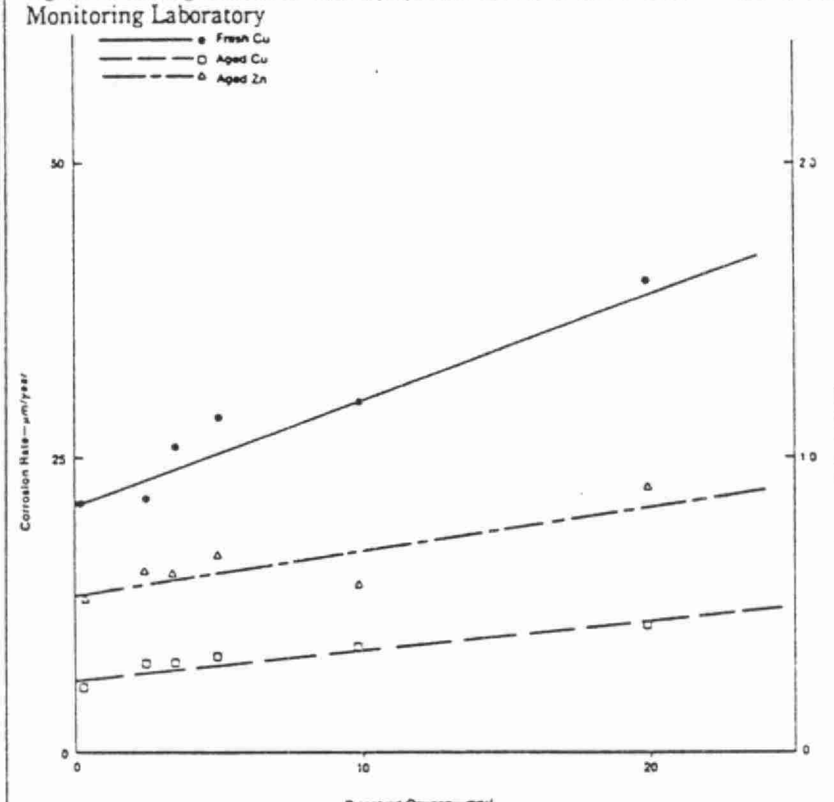

Figure 4. Corrosion rate of three metal surfaces versus dissolved oxygen *(baseline parameters: temperature—11.2 ± 1.2°C; flow—5.4 ± 0.2 cm/s; pH—7.00 ± 0.07; conductivity—149 ± 22 µS/cm; turbidity—1.9 ± 0.7 ntu; Cl residual—0 mg/L)*

Results and discussion

Dissolved oxygen. Oxygen functions as the primary electron acceptor in many corroding systems. For this reason, it is possible for O_2 to be the rate-limiting reactant and for an increase in dissolved O_2 to substantially increase the corrosion rate. Dissolved O_2 in a water supply can vary considerably, depending on the water source, the water temperature, and the treatment process sequence.

The dissolved O_2 concentration was varied by bubbling gas mixtures of nitrogen (N_2) and O_2 through the recirculating reservoir to obtain concentrations from 0 to 20 mg O_2/L. In these experiments, the corrosion rates of all three surfaces increased by 50-100 percent as the concentration of dissolved O_2 increased (Figure 4), with the increase being somewhat greater for fresh copper than for aged copper or zinc. The results suggest that O_2 is a rate-determining reactant in the corrosion of both Cu and Zn. The results are consistent with the limitation being either O_2 diffusion through the oxide film or the rate of the O_2 reduction reaction.

The significance of the dissolved O_2 effect in Seattle is small because the O_2 concentration is always near saturation. The results indicate that corrosion rates would decrease if the O_2 concentration was lowered significantly.

Free chlorine residual. Chlorine, the disinfectant of choice for most water systems in the United States, is a strong oxidizing agent and can act as an electron acceptor in the corrosion process. Atlas et al[4] reported that Cl had a greater effect on Cu corrosion than did dissolved

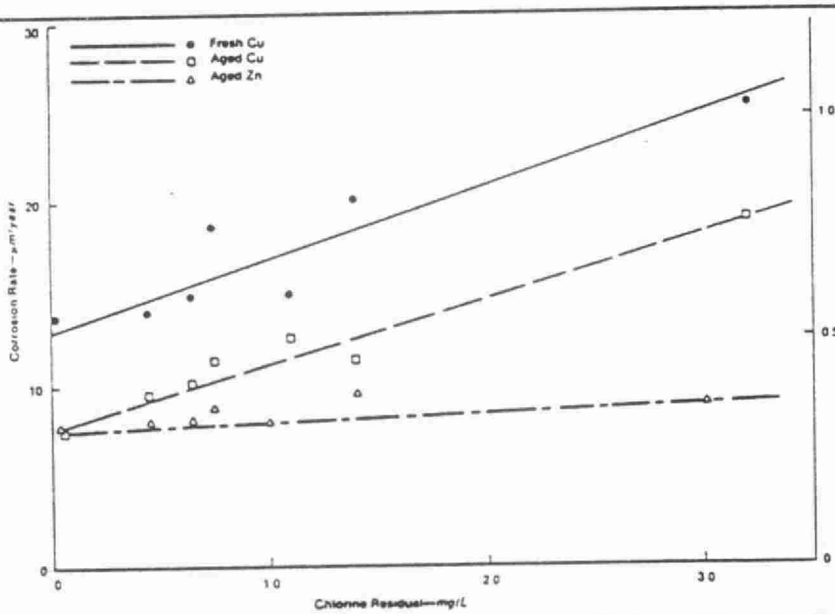

Figure 5. Corrosion rate of three metal surfaces versus chlorine residual *(baseline parameters: temperature—12.8 ± 0.9°C; flow—5.8 ± 0.1 cm/s; pH—7.0 ± 0.5; conductivity—39 ± 22 µS/cm; turbidity—0.3 ± 0.02 ntu)*

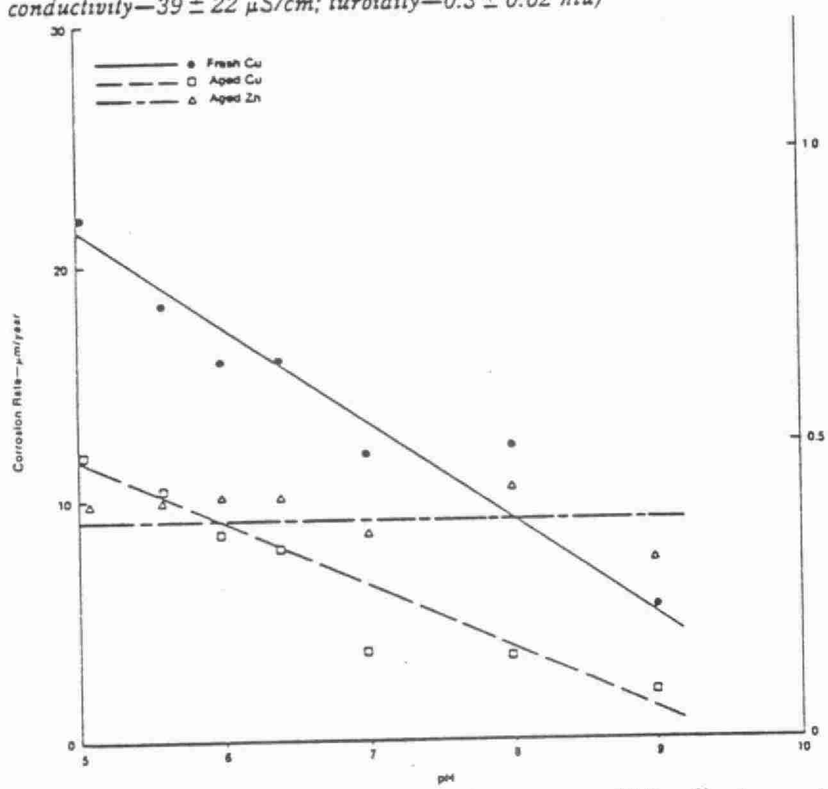

Figure 6. Corrosion rate of three metal surfaces versus pH *(baseline parameters: temperature—15.2 ± 0.8°C; flow—5.5 ± 0.2 cm/s; turbidity—0.6 ± 0.2 ntu; dissolved O_2—10.3 ± 0.5 mg/L; Cl residual—0 mg/L)*

O_2. In the current experiments, when Cl residual was varied using sodium hypochlorite and sodium sulfite, the Cl residual influenced the corrosion rate of Cu considerably but had almost no effect on the corrosion rate of Zn (Figure 5).

The change in corrosion rate for the Cu systems was roughly the same with 1 mg free Cl residual/L or with 10 mg dissolved O_2/L. Although the corrosion rates for the O_2 and Cl tests are not directly comparable because conductivities differed, it appears that both oxidizing agents significantly affect Cu corrosion rates and that O_2 has a greater effect on Zn corrosion rate than does Cl.

To put these rates in a different perspective, a Cu corrosion rate of 20 µm/year corresponds to the transfer of 1.5×10^{-6} µelectron equivalents/cm²-day for conversion of Cu(m) to Cu^{2+}, or 3.1×10^{-3} electron equivalents/L-day in 0.75-in. (20-mm) copper tubing. If all the oxidizing capacity were provided by free Cl, the Cl would be depleted at a rate of 0.038 mg/L-min. The corresponding value for O_2 depletion is 0.017 mg/L-min. At such a rate, all the free Cl in a distribution water could be consumed after a few minutes of exposure to household plumbing. Because of the higher concentration of O_2 in source waters and its lower rate of consumption, depletion of all the O_2 in distribution water would take several hours to a few days. For corrosion of iron, the depletion rates would be slightly different (because of the difference in densities and equivalent weights of Cu and iron) but comparable. In the larger-diameter pipes of the distribution network, depletion rates would be approximately an order of magnitude slower.

These calculations provide a perspective on corrosion rates from the viewpoint of oxidant depletion, a viewpoint that is rarely considered explicitly. Although the actual corrosion rates in distribution and household plumbing may be lower than 20 µm/year, especially in the presence of a protective film, this value is reasonable for new plumbing materials and for older materials that lack significant scale deposition. Under such conditions, corrosion reactions can readily deplete a disinfectant residual in small-diameter pipes with intermittent flow.

pH. Seattle's corrosion control program includes the increase of the pH and alkalinity of the water. As expected, the corrosion rate decreased as the pH was increased (Figure 6). When the pH was increased from 6 to 8, the corrosion rate of fresh Cu decreased by almost 50 percent, which approximates the change being effected by Seattle's chemical addition program. The corrosion rate of aged Cu decreased by an even larger fraction over the same pH range. However, there was almost no change in the corrosion rate of the zinc electrode over the entire pH range studied (5.0–9.0).

Flow rate. The flow rate through a home plumbing system can vary considerably, depending on the time of the day and other factors. An increase in corrosion rate with increased flow rate might be expected because of a lowering of the diffusional resistance in the liquid layer near the pipe wall. Initially, when low flow rates were studied in the CRM sample cell, no change in corrosion rate with flow was found (Figure 7). A modified cell was then constructed in a pipe section,[5] and measurements were made at flow rates one hundred times greater (Figure 8). Again, there was no change in corrosion rate with increasing flow. It was impossible to obtain a sufficiently high flow to produce a significant change in corrosion rate, suggesting that diffusion of reactants or products though the liquid film was not rate limiting within the range of flows investigated.

Temperature. The water temperature in the Seattle area fluctuates from a low of about 41°F (5°C) in the winter to a high of 68°F (20°C) in the summer. Experiments were conducted over much of this range by heating or cooling the water in the recirculating reservoir. Results presented in Figure 9 show that for the aged surfaces a substantial change in corrosion rate occurred with an increase in temperature. The corrosion rate increased by about 50 percent when the temperature changed from 50 to 77°F (10 to 25°C). There is too much scatter in the results for fresh Cu for a trend to be discerned.

To some extent corrosion may be a seasonal problem. As the temperature increases, so do the rates of the chemical oxidation and reduction reactions involved in corrosion. The formation and dissolution rates of the oxides as well as their equilibrium solubility also change with temperature. In addition, the transport rate of products and reactants across the interface increases as temperature increases. The greater the supply of reactants, the greater would be the dissolution of the pure metals and the greater the corrosion rate. Although the overall effect of temperature was clear for corrosion of Zn and aged Cu, it was not possible to identify the critical step that was being affected.

Conductivity. Three ions were selected for study: chloride (Cl^-), sulfate (SO_4^{2-}), and bicarbonate (HCO_3^-). Data were collected for each salt as the conductivity was incrementally increased from very low values to near 1000 μS/cm. The results of two complete sequences for changes in SO_4^{2-} and Cl^- and one sequence for changes in HCO_3^- are presented in Figures 10–12.

In all cases the corrosion rate increased with increasing conductivity, although the relative rate of change for the Cu electrodes diminished at conductivities of >100–200 μS/cm. It was found that for a given conductivity, the corrosion rate was always greatest with Cl^- and least with HCO_3^-. The effect of SO_4^{2-} seemed to mimic that of Cl^- with the aged electrodes and that of HCO_3^- with the cleaned electrode.

For the Cl^- and SO_4^{2-} salts, the pH increased steadily from about 6.3 to 7.0 during the experiments. The pH change probably reduced moderately the effects of conductivity. For the HCO_3^- a more pronounced increase in pH was experienced (6.3 to 7.9), which may have had a larger damping effect on the corrosion rates at high conductivities than that found with Cl^- and SO_4^{2-} ions. If corrections were based on the pH effects in Figure 6, the corrosion rates at low conductivity would be unchanged and the rates at high conductivity would be increased by 20–30 percent or more. The effects of HCO_3^- were of particular

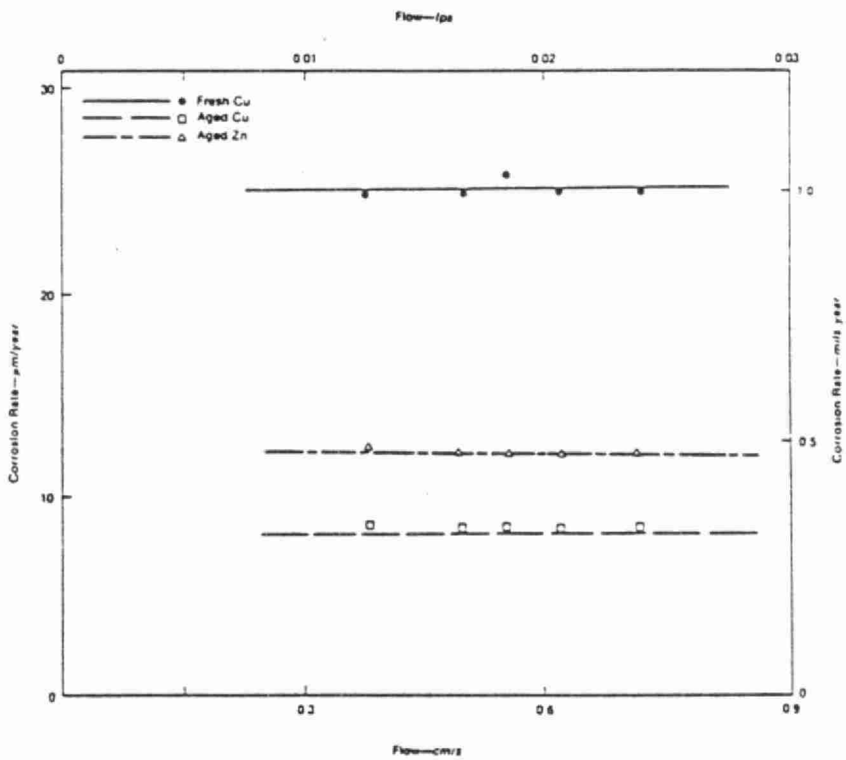

Figure 7. Corrosion rate of three metal surfaces versus flow rate *(baseline parameters: temperature—12.2 ± 0.2°C; pH—7.3 ± 0.1; conductivity—55 ± 6 μS/cm; turbidity—0.63 ± 0.03 ntu; dissolved O_2—10.5 ± 0.2 mg/L; Cl residual—0 mg/L)*

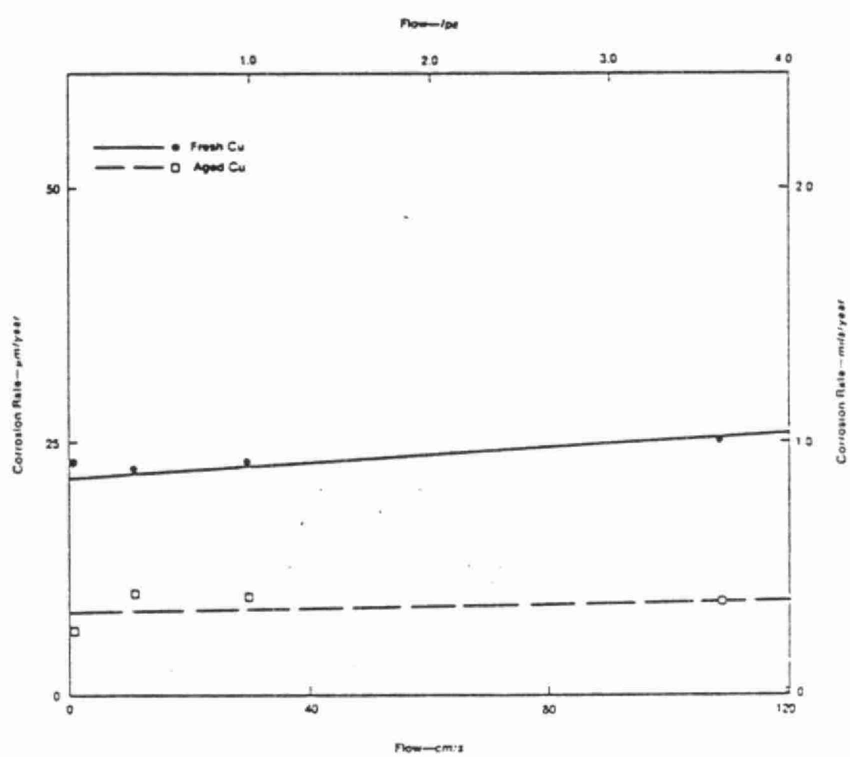

Figure 8. Corrosion rate of two metal surfaces versus flow rate *(baseline parameters: temperature—15 ± 0.7°C; pH—7.1 ± .06; conductivity—116 ± 12 μS/cm; dissolved O_2—saturated; Cl residual—0 mg/L)*

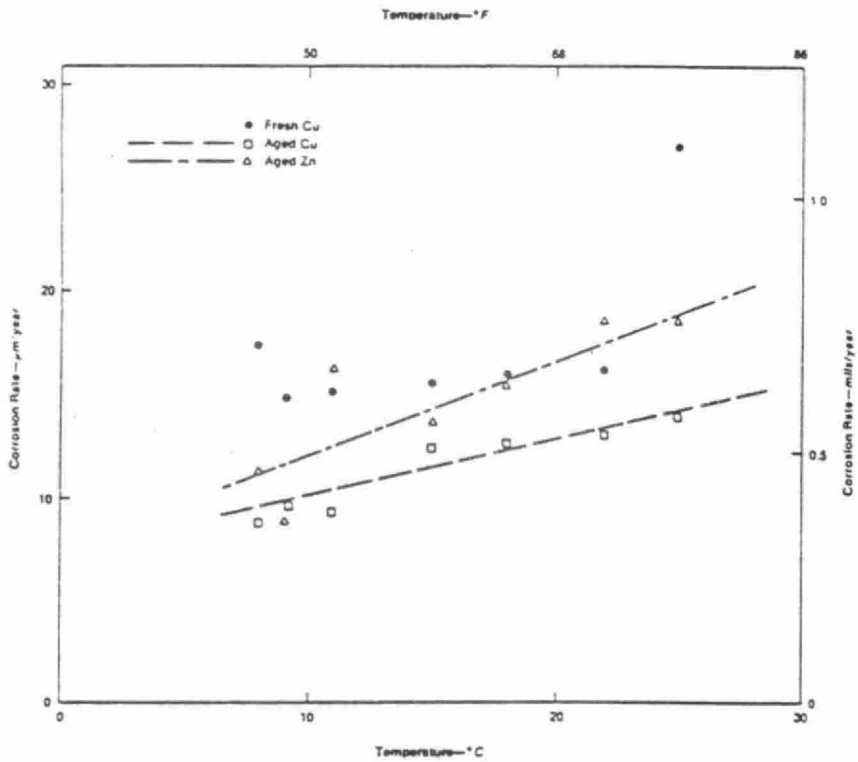

Figure 9. Corrosion rate of three metal surfaces versus temperature *(baseline parameters: flow—5.7 ± 0.8 cm/s; pH—7.0 ± 0.05; conductivity—80 ± 44 μS/cm; turbidity—0.9 ± 0.5 ntu; dissolved O_2—9.6 ± 0.85 mg/L; Cl residual—0 mg/L)*

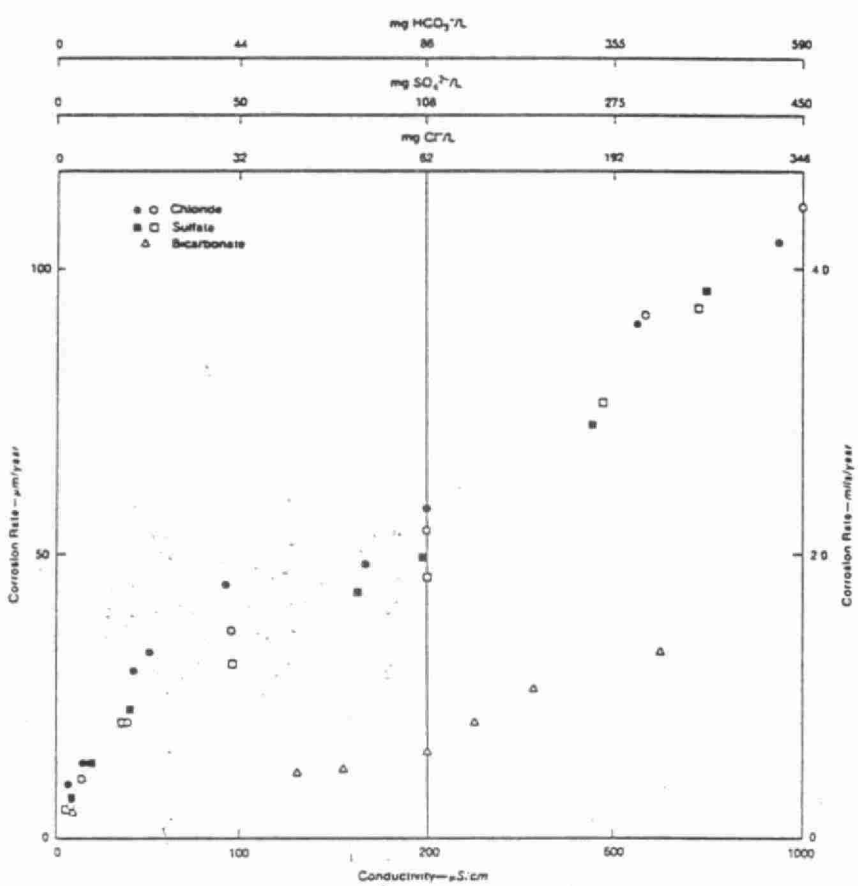

Figure 10. Corrosion rate of aged zinc versus solution conductivity for three ions *(baseline parameters: temperature—11.1-18.2°C; flow—5.4-5.8 cm/s; pH—6.2-7.8; turbidity—0.18- 0.8 ntu; dissolved O_2—10.2-11.3 mg/L; Cl residual—0 mg/L)*

interest because increased alkalinity is sometimes equated with increased corrosion resistance. Although this may be valid if the effects of alkalinity are primarily to buffer the pH near the surface or to cause precipitation of a protective carbonate film, or both, the present results emphasize that in some circumstances the dominant effect of adding alkalinity may be to increase corrosion by increasing conductivity.

The results are not amenable to simple interpretation, either for varying concentrations of a single ion or for comparing the effects of the different ions. A wide range of interactions may occur between the anions and parts of the corroding system. Besides increasing the concentration of charge carriers in the interfacial region, any of these ions may adsorb onto the film or the corroding metal surface and change their structure or charge-transfer rates. Furthermore, HCO_3^- may precipitate in the interfacial region or may alter the corrosion rate by buffering the interfacial pH. Further study is needed before the importance of each mechanism involved can be understood and quantified.

Summary and conclusions

The corrosion rate of common plumbing materials was investigated as a function of physical and chemical water quality characteristics. For the systems studied, changes in dissolved O_2, conductivity, and temperature had a moderate effect on the corrosion rate of both Cu and Zn, whereas pH and Cl residual affected Cu corrosion rates but not those of Zn. Increases in conductivity up to about 200 μS/cm increased Cu corrosion rates significantly but generally had less effect at higher values. Zinc corrosion rates increased with conductivity up to 1000 μS/cm. For equal conductivities, corrosion rates were greater in systems with Cl^- than in systems with HCO_3^-; SO_4^{2-} had an effect equivalent to Cl^- on aged Cu and Zn electrodes but equivalent to HCO_3^- on fresh Cu. Flow rate had almost no effect on the corrosion rate of either metal.

Aged and fresh Cu electrodes responded in a qualitatively similar manner to changes in water quality, although different corrosion rates were reached. Fresh Cu, lacking a thick protective oxide film, corroded at a much greater rate than did aged Cu. The results suggest that both transport of reactants through an oxide film and the reaction rates at the interface exert control over corrosion rates in tap water. Because the aged Cu surface is more representative of Cu tubing in homes, most water distribution systems should be at least partially protected from a high corrosion rate by their oxide film.

Zinc corrosion rates appeared to respond less dramatically to changes in

water quality, other than conductivity, than those of Cu. This may have been a result, at least partially, of the relatively thick oxide film that developed on the Zn electrode.

The linear polarization technique appears to be a reliable method for monitoring nearly instantaneous changes in corrosion brought about by changes in water quality. The fact that linear polarization gives these values within hours instead of months (the typical duration of coupon tests) is a major advantage of the analytical technique.

Acknowledgment

The Mobile Water Quality Monitoring Laboratory has been used under cooperative agreement CR-810508-02-3 with the US Environmental Protection Agency. Marvin Gardels, project officer for that grant, assisted the research. Stein Osterhus was supported by the Valle Scandinavian Exchange Program during his graduate study at the University of Washington.

References

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2. STERN, M. & GEARY, A.L. Electrochemical Polarization: I. A Theoretical Analysis of the Shape of Polarization Curves. *Jour. Electrochem. Soc.*, 104:1:56 (1957).
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4. ATLAS, D.; COOMBS, J.; & ZAJICEK, O.T. The Corrosion of Copper by Chlorinated Drinking Waters. *Water Res.*, 16:5:693 (1982).
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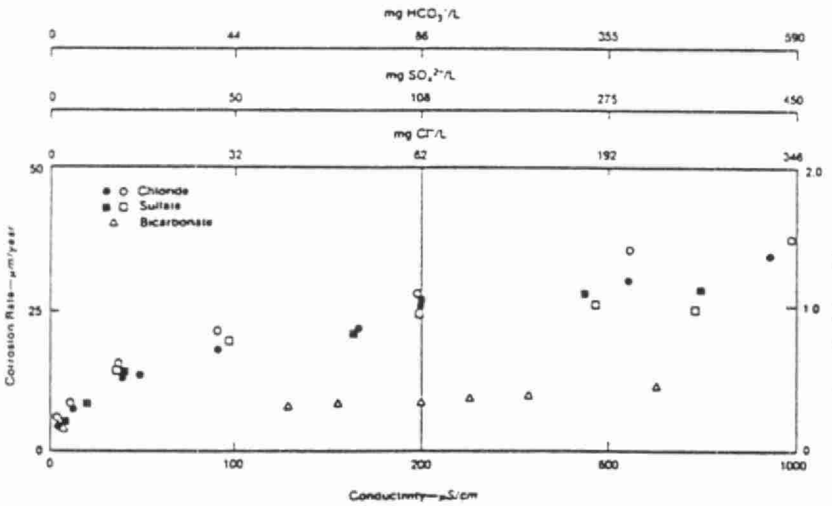


Figure 11. Corrosion rate of aged copper versus solution conductivity for three ions *(baseline data identical to those in Figure 10)*

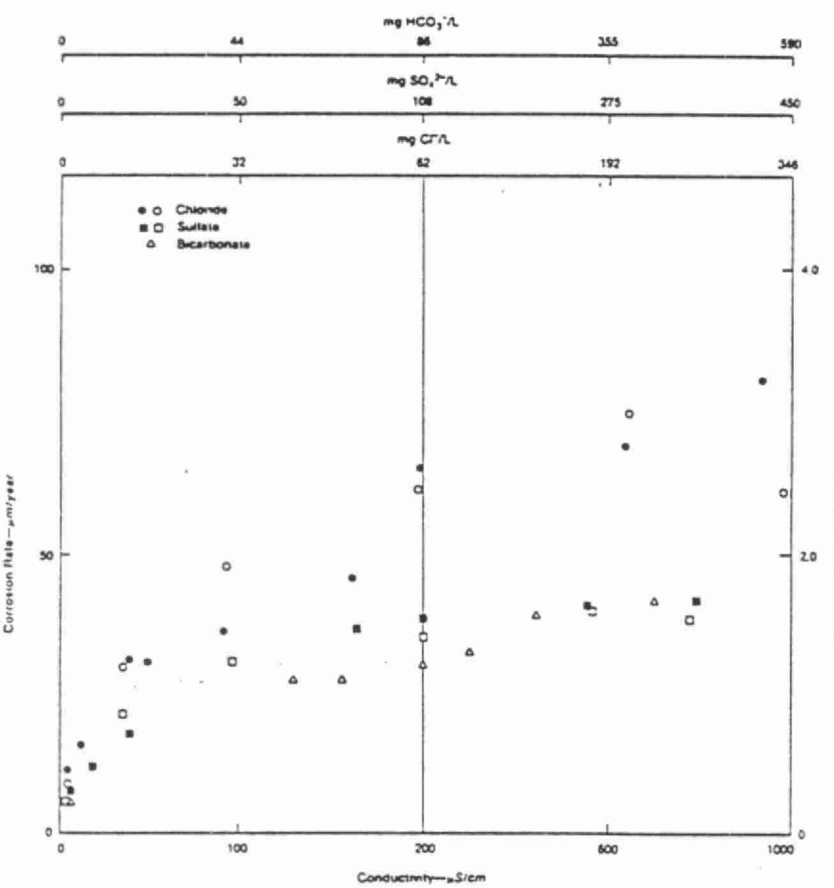


Figure 12. Corrosion rate of fresh copper versus solution conductivity for three ions *(baseline data identical to those in Figure 10)*

About the authors: *At the time of the work described in this article, Al Stone and Stein Osterhus were graduate students in the Environmental Engineering and Science Program, Department of Civil Engineering, University of Washington, More Hall FX-10, Seattle, WA 98195. Stone, who received his undergraduate degree in chemistry from Rensselaer Polytechnic Institute, Troy, N.Y., is currently spending a year at the Central Institute for Industrial Research, University of Oslo, Norway, as part of the Valle UW/Scandinavian Exchange Program. John Ferguson is a professor, Dimitris Spyridakis and Mark Benjamin are associate professors, and Steve Reiber is a research assistant professor in the Department of Civil Engineering, University of Washington.*

EMERGING WATER SUPPLY TECHNOLOGY　　AWWARF Code #: US-16

PROJECT DESCRIPTION

Project Title:

Radon in Well Supplies: Occurrence and Removal

Contact (name of person, organization, address, telephone):

Ramon G. Lee
Director, Research & Technology
American Water Works Service Co. Inc.
1025 Laurel Oak Road
Voorhees, N.J. 08043
(609) 346-8335

Project Description (Please attach a schematic diagram if appropriate):

EPA has classified Radon as a cancer causing substance. The primary risk from exposure to Radon arises from inhalation of the gas, some of which originates as a result of the transfer from drinking water to indoor air. EPA estimates that Radon liberated from drinking water consititutes, on average, only 2 to 5 percent of the indoor air Radon level.

In preparation to achieve compliance with the forthcoming regulations, an analytical Radon survey of well supplies throughout the American Water Works System was performed. The survey was designed to determine the levels of Radon in individual well supplies and to provide an assessment of the effects of existing treatment and operating practices on Radon levels.

The range of detected Radon concentrations in 377 well supplies (15 states) across the American System was <100 pCi/L to 4853 pCi/L. The systemwide mean Radon concentration was 686 pCi/L and the median Radon concentration was 320 pCi/L.

Aeration was found to be very effective in the removal of Radon from drinking water. Packed tower aerators achieved greater than 95 percent reduction while conventional tray aerators attained greater than 75 percent reduction in Radon concentrations.

This report presents the results of the Radon Survey and in addition, provides pertinent information on the sources and characteristics of Radon; the health effects associated with exposure to Radon; analytical techniques for the measurement of Radon, and; EPA's approach to regulating Radon in Drinking Water.

EMERGING WATER SUPPLY TECHNOLOGY

AWWARF Code #: US-17

PROJECT DESCRIPTION

Project Title:

A Study of Possible Economical Ways of Removing Radium from Drinking Water

Contact (name of person, organization, address, telephone):

Richard P. Lauch, Environmental Engineer
Inorganic and Particulate Control Branch
Drinking Water Research Division
Water Engineering Research Laboratory
U.S. EPA
Cincinnati, OH 46268, USA
Tel: (513) 569-7237

Project Description (Please attach a schematic diagram if appropriate):

The primary objectives of this study were to determine the variables that control the removal of radium during the iron and manganese removal process and to evaluate the possibility of exploiting these factors to provide an inexpensive means of removing radium, using existing or modified iron removal facilities. This study investigated how water chemistry influences Ra-226 sorption to iron and manganese oxides and sorption to filter sand.

Operating and cost data (including data on efficiency, results, etc.):

Batch studies using freshly precipitated iron oxides, formed in the laboratory, showed that sorption of radium from typical groundwaters would result in maximum removal of 10 to 20% and would usually be much less. Radium removals obtained by freshly precipitated hydrous manganese oxides in batch studies were much greater than those obtained in systems containing only iron oxides.

Filter sand has a potential capacity to sorb a significant concentration of radium at typical hardness concentrations if the capacity is maintained by periodically rinsing the sand with a dilute acid.

Place(s) of installation/application (including dates):

This research was conducted during 1983 to 1986 at the University of Iowa Hygienic Laboratory, Iowa City, Iowa and Pilot Plant at Oxford, Iowa.

Patent staus, if applicable:

NONE

Other information (e.g., funding source, cooperating agencies, etc.):

The Drinking Water Research Division Project Officer is Richard P. Lauch and the project is being conducted as a cooperative agreement with the University of Iowa, Iowa City, Iowa. The Principal Investigator at the University of Iowa is Dr. Richard L. Valentine.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

EMERGING WATER SUPPLY TECHNOLOGY

AWWARF Code #: US-18

PROJECT DESCRIPTION

Project Title:

STUDY OF RESIDUALS MANAGEMENT AT WATER TREATMENT PLANTS

Contact (name of person, organization, address, telephone):

Richard P. Lauch, Environmental Engineer
Inorganic and Particulate Control Branch
Drinking Water Research Division
Water Engineering Research Laboratory
Cincinnati, OH 45268, USA
Tel: (513) 569-7237

Project Description (Please attach a schematic diagram if appropriate):

A full scale well water treatment plant for a small community was evaluated for radium removal. The plant consists of iron removal, using aeration, filtration and settling; hardness and radium removal, using ion exchange; and radium removal from the waste brine using the Dow Radium Selective Complexer (RSC). The purpose of this research was to determine the effectiveness of each stage for radium removal.

Operating and cost data (including data on efficiency, results, etc.):

Results showed that very little radium was removed across the iron removal process. Radium was removed to concentations below the MCL with ion exchange and as expected, hardness broke through before radium. Greater than 99% of the radium was removed from the waste brine by the RSC.

Place(s) of installation/application (including dates):

The research was performed from 1984 to 1987.

The water treatment plant was located at:
Redhill Forest Homeowners Association
Hartsel, CO.

Patent staus, if applicable:

NONE

Other information (e.g., funding source, cooperating agencies, etc.):

The Drinking Water Research Division Project Officer was Richard P. Lauch and the project was conducted as a cooperative agreement with the Redhill Forest Association, Hartsel, Colorado. The Principal Investigator was Dr. Kenneth A. Mengelson of Rocky Mountain Consultants, Denver, CO.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

EMERGING WATER SUPPLY TECHNOLOGY

AWWARF Code #: US-19

PROJECT DESCRIPTION

Project Title:

Selective Removal of Radium from Drinking Water

Contact (name of person, organization, address, telephone):

Richard P. Lauch, Environmental Engineer, Inorganic and Particulate Control Branch, Drinking Water Research Division, Water Engineering Research Laboratory, U.S. EPA, Cincinnati, OH45268. Tel 513-569-7237.

Project Description (Please attach a schematic diagram if appropriate):

Manganese dioxide coated filter sorbers were tested for removing radium from waters that contained high and low hardness concentrations.

Operating and cost data (including data on efficiency, results, etc.):

A ten-inch MnO_2 filter sorber, treated 800 ft^3 of water containing high hardness and reduced the radium concentration from 37 pCi/L to below Maximum Contaminant Level (MCL) of 5 pCi/L. Another ten-inch MnO_2 filter sorber treated 1000 ft^3 of water containing low hardness and reduced radium from 13 pCi/L to below the MCL. Testing also showed some sorption of other metals including cadmium, calcium, cesium, chromium, cobalt, iron, manganese, and sodium.

The filters were coated by circulating a hot $KMnO_4$ solution through the filters. Testing showed that no acrylic fiber or manganese were leached off the filter into the product water.

Place(s) of installation/application (including dates):

Manganese dioxide filter sorber testing was conducted between 1984 and 1986 at North Carolina State University, Raleigh, N.C., Highland Park, N.C. and Gateway Mobile Home Park, N.C.

Patent staus, if applicable:

NONE

Other information (e.g., funding source, cooperating agencies, etc.):

The Drinking Water Research Division Project Officer is Richard P. Lauch and the project is being conducted as a cooperative agreement with North Carolina State University, Raleigh, N.C. The Principal Investigator at North Carlina State University is Dr. Edward P. Stahel.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

EMERGING WATER SUPPLY TECHNOLOGY

AWWARF Code #: US-20

PROJECT DESCRIPTION

Project Title:

Radon Removal Techniques for Community Water Supplies

Contact (name of person, organization, address, telephone):

Kim R. Fox, Drinking Water Research Division, Water Engineering Research Laboratory, U.S. EPA, Cincinnati, OH 45268. Tel: (513) 569-7820

Project Description (Please attach a schematic diagram if appropriate):

This project will evaluate the practical application of two techniques for removing radon from drinking water; granular activated carbon treatment and aeration (diffused and packed tower). Recent studies have demonstrated the feasibility of both treatment techniques for removing radon from single family homes, but this research project will study the application to a larger central treatment plant. The treatment processes will be installed in two small communities having central water systems. One community will install parallel systems of GAC and aeration treating a drinking water with >100,000 pCi/L radon. The other small community will install GAC and aeration for treating the water with 40,000 pCi/L radon. The project will evaluate treatment efficacy, costs, operation and maintenance, and the design aspects of upgrading a small community central treatment plant. The U.S. EPA is mutually interested in the results of this study to increase the data base for future regulations regarding the setting of an MCL for radon. The state of New Hampshire has an urgent need to study these treatment techniques for radon removal because many bedrock wells in that state have experienced radon gas levels of 10,000 to 100,000 pCi/L.

In addition to the original work above, this project has been expanded to look at low cost/low technology aeration techniques for radon removal and to look at point-of-entry application for radon reduction in a home.

Operating and cost data (including data on efficiency, results, etc.):

An economic analysis will be conducted to compare the construction, operation and maintenance costs in relation to specific radon gas concentrations, water system demands and other possible variables. The analysis will define thresholds of key parameters (for example, radon concentration or system demand) at which the cost-effectiveness of a treatment technique might change.

Place(s) of installation/application (including dates):

State of New Hampshire -- University of New Hampshire

Two sites have been selected in New Hampshire in the vicinity of the University. 9/1/85 - 5/30/88

Patent staus, if applicable:

NONE

Other information (e.g., funding source, cooperating agencies, etc.):

Cooperative Agreement: U.S. EPA and New Hampshire Water Supply and Pollution Control Commission, CR812602

Principal Investigator: Harry Stewart, State of New Hampshire

Project Officer: Kim R. Fox, U.S. EPA, WERL

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

EMERGING WATER SUPPLY TECHNOLOGY — AWWARF Code #: US-21

PROJECT DESCRIPTION

Project Title:

Jar-Filter Coagulant Test

Contact (name of person, organization, address, telephone):

David Hendricks
Engineering Research Center
Colorado State University
Fort Collins, CO 80523
(303) 491-8273

or

Deborah R. Brink
AWWA Research Foundation
6666 W. Quincy Avenue
Denver, CO 80235
(303) 794-7711 ext. 6011

Project Description (Please attach a schematic diagram if appropriate):

The conventional jar test is not applicable to low turbidity waters, e.g., those having turbidity levels <1 NTU because the additional coagulants do not form settleable flocs. Low turbidity waters have been neglected, however, as a concern in filtration research and practice because already they meet drinking water standards. The _Giardia_ problem has resulted in attention on the filtration problems of these water.

The jar filter test is comprised of the addition of six bench scale filters to use in conjunction with the jar test. The research has prescribed a standard design and standard procedures for the test, and has documented its validity by comparisons with pilot plant data.

Operating and cost data (including data on efficiency, results, etc.):

The bench scale filters are small columns about 5 cm diameter by about 60 cm long, filled with media from the operating full scale filters. The results give L-shaped or U-shaped turbidity dose curves that correspond approximately with pilot plant results.

Place(s) of installation/application (including dates):

No known installations through the Las Vegas filtration plant has used such a set-up for many years (learned subsequent to completion of research).

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

Colorado State University Experiment Station.
Work done in conjunction with EPA project 1981-84.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

EMERGING WATER SUPPLY TECHNOLOGY　　　　AWWARF Code #: US-22

PROJECT DESCRIPTION

Project Title:

Rapid Rate Filtration of Low Turbidity Waters

Contact (name of person, organization, address, telephone):

David W. Hendricks, Ph.D., Professor
Engineering Research Center
Foothills Campus
Colorado State University
Fort Collins, CO 80523
(303) 491-8273

Project Description (Please attach a schematic diagram if appropriate):

Rapid rate filtration of low turbidity waters, i.e. waters having turbidity levels <1.0 NTU, has not been given attention in filtration research or practice until the Giardia cyst problem appeared on the scene. In usual practice, the filtration of low turbidity waters was given only token attention since the input turbidities already were less than the 1.0 NTU drinking water standard and any filtration resulted in some improvement. The problem had three elements: (1) perception that a problem existed, (2) having a measurement of filtration efficiency, and (3) determining how to effectively filter low turbidity water.

Results of EPA sponsored research at Colorado State University, 1981-84, showed that removals of $\geq$ 70 percent turbidity or $\leq$ 0.10 NTU turbidity resulted in effective filtration to give > 99.9 percent Giardia cyst removal and > 99.9 percent coliform removal, when raw water turbidities were about 0.5 NTU. Efficient filtration could occur, however, only when coagulation was "optimum," which required selection of coagulants and determination of dosages to give effective filtration.

Operating and cost data (including data on efficiency, results, etc.):

The cost of using effective coagulants at optimum dosages is more expensive than the practice of using no chemicals or "token" chemical coagulation. Without "proper" coagulation, however, the capital investment, i.e. the filtration plant, is wasted.

Place(s) of installation/application (including dates):

Several filtration plants are employing "proper" chemical coagulation.

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

EPA sponsored research at Colorado State University, 1981-84.
AWWARF sponsored research at Colorado State University.
Cooperating organizations were CH2M Hill, City of Fort Collins, Colorado Health Department.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

EMERGING WATER SUPPLY TECHNOLOGY

AWWARF Code #: US-23

PROJECT DESCRIPTION

Project Title:

Design and Operation Guidelines for the Optimization of the High Rate Filtration Process

Contact (name of person, organization, address, telephone):

John L. Cleasby, Ph.D., Professor
Civil Engineering Department
Iowa State University
492 Town Engineering Bldg.
Ames, IA 50010
(515) 294-4978

Project Description (Please attach a schematic diagram if appropriate):

Through an initial survey of the design and operational characteristics of existing rapid rate filtration plants currently able to consistently produce a high quality effluent, e.g. turbidity less than 0.1 ntu, the investigators will identify key parameters that contribute directly to filtration effectiveness. Pilot plant research to further evaluate and quantify the effect of these parameters on finished water quality will then be performed. Survey and pilot scale research results will be validated through incorporation of the operation and process design results into full-scale plants. This research will result in the development of guidelines for the design and operation of surface water high rate filtration plants capable of consistently producing high quality finished water. Guidelines for modifying existing plant processes and operations, as well as for the design of new treatment facilities will be included, along with estimates of the attendance costs.

The project commenced in August 1987 and will continue through August 1989.

Operating and cost data (including data on efficiency, results, etc.):

Place(s) of installation/application (including dates):

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

$175,000 AWWARF funding
$109,000 Iowa State University and Bohon and Menk, Inc.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

EMERGING WATER SUPPLY TECHNOLOGY

AWWARF Code #: US-24

PROJECT DESCRIPTION

Project Title:

Biological Denitrification of Groundwater

Contact (name of person, organization, address, telephone):

Mr. Richard W. Hansen
General Manager/Chief Engineer
Three Valleys Municipal Water District
P.O. Box 1300
Claremont, CA 91711
(714) 621-5568

Project Description (Please attach a schematic diagram if appropriate):

This project will evaluate the use of fluidized bed reactors for biological denitrification of drinking water at both the pilot- and full-scale level (see attached schematic). Optimal operational criteria, process reliability, and operator requirements will be determined. Extensive water quality testing of the process effluent will be undertaken. Economic, design, and performance results for the fluidized bed system will be compared to those obtained from a rotating biological contactor system treating identical water.

The project began June 1, 1987 and will continue until January 31, 1989. A final report on the project is expected to be available by mid-1989.

Operating and cost data (including data on efficiency, results, etc.):

Not available at this time.

Place(s) of installation/application (including dates):

Three Valleys Municipal Water District, Claremont, CA

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

$80,000 AWWARF funding
$74,000 Three Valleys Municipal Water District and Engineering-Science, Inc.

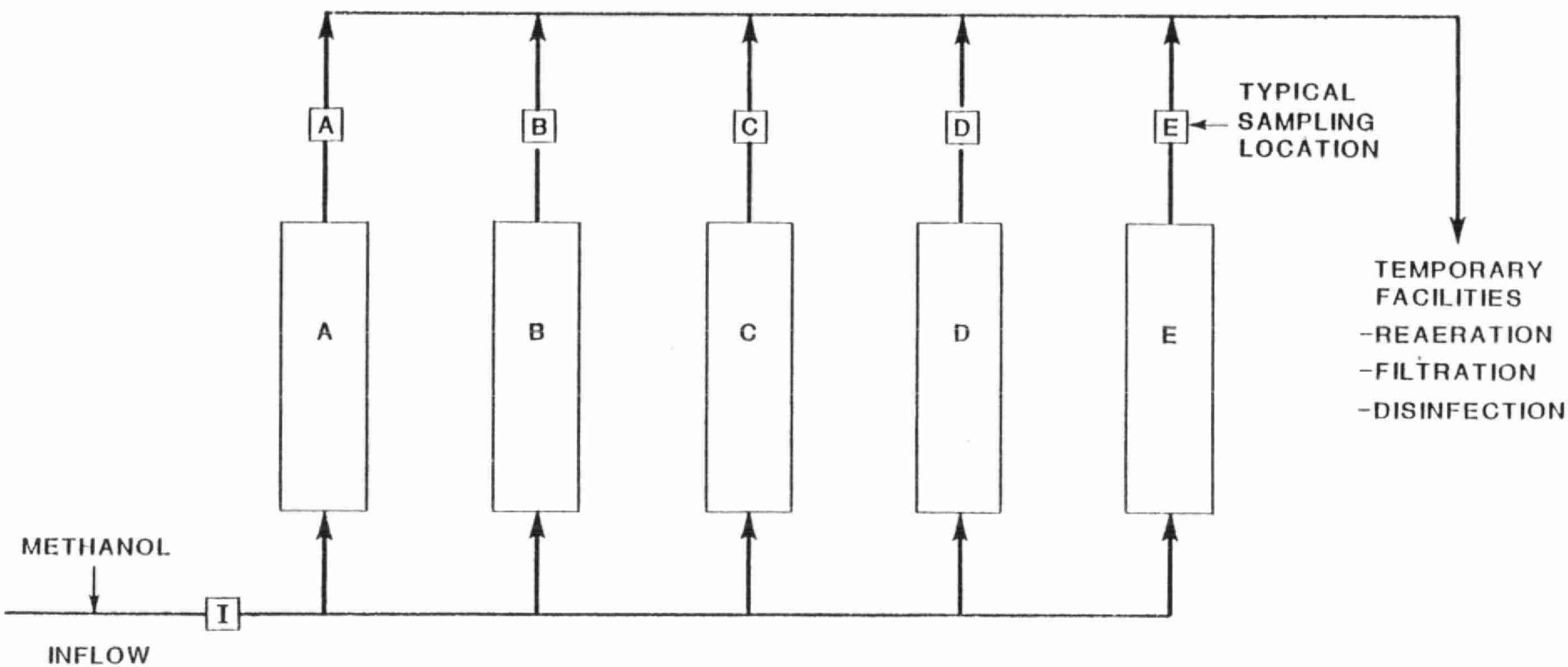
If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

US-119

FLUIDIZED BED REACTOR

PARAMETRIC TEST PHASE

SYSTEM CONFIGURATION FOR UPFLOW COLUMNS



NOTE: EFFLUNT SAMPLES WILL BE FILTERED
IN THE LABORATORY AS REQUIRED

ENGINEERING-SCIENCE

FIGURE B-1

FLUIDIZED BED REACTOR

PROOF TESTING PHASE

SYSTEM CONFIGURATION FOR UPFLOW COLUMNS

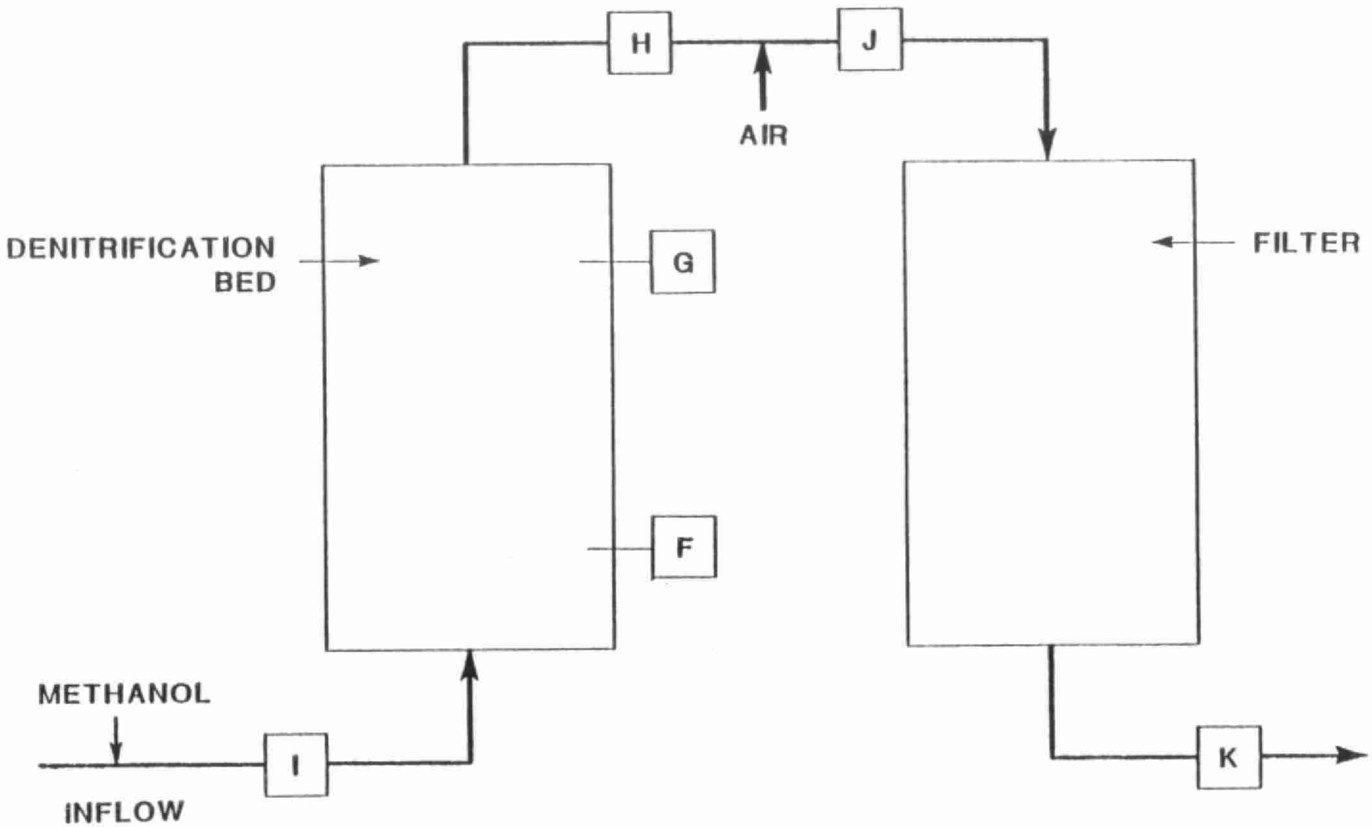


FIGURE B-2

EMERGING WATER SUPPLY TECHNOLOGY AWWARF Code #: US-25

PROJECT DESCRIPTION

Project Title: "Use of Membrane Technology to Remove Organics from Small Systems" - A cost and performance evaluation of membrane technology (ultrafiltration) to remove organics from small systems serving less than 10,000 population.

Contact (name of person, organization, address, telephone):

Dr. James S. Taylor, P.E.
CEES Department
The University of Central Florida
Orlando, Florida 32816
(305) 275-2785

Project Description (Please attach a schematic diagram if appropriate):

Phase I: (1) Locate water utilities in Florida serving less than 10,000 population with substantial THM problem, (2) Evaluate sites and select one groundwater and one surface water site, (3) Conduct bench-scale studies to select appropriate membrane and establish pretreatment necessary to maintain adequate membrane flux for long-term operation, (4) Develop detailed work plans for conduct of long-term pilot-scale studies.

Phase II: Collect cost and performance data from the 10gpm pilot-scale membrane system for approximately one year at each of the two selected sites. Also, investigate options for the disposal of reject waters at each site.

Phase III: Prepare final project report and project summary. Prepare journal articles on selected portions of the project for submission to peer-reviewed journals.

Operating and cost data (including data on efficiency, results, etc.):
As of July 15, 1987, the pilot-scale system has operated for 3500+ hours (non-continuous) at the groundwater test site. Permeate flow averaged 7.6 gpm and recovery averaged 73 percent during this period. Average values for other parameters (raw, finished, percent rejection) include:

Total Dissolved Solids: 578 mg/L, 121 mg/L, 79%
Total Hardness: 355 mg/L, 32 mg/L, 91%
Calcium Hardness: 312 mg/L, 35 mg/L, 89%
Alkalinity: 328 mg/L, 34 mg/L, 90%
Color: 30 cpu, 2 cpu, 93%
Dissolved Organic Carbon: 10.9 mg/L, 2.1 mg/L, 81%
Total Organic Halide
Formation Potential: 1,000 ug/L, 37 ug/L, 96%
Trihalomethane
Formation Potential: 455 ug/L, 22 ug/L, 95%

Cost data have not been evaluated at this point in the project.

Place(s) of installation/application (including dates):
Groundwater test site: Flagler Beach, Florida (Nov. 1986 - Oct. 1987)

Surface Water test site: Punta Gorda, Florida (Nov. 1987 - Oct. 1988)

Patent staus, if applicable:
N/A

Other information (e.g., funding source, cooperating agencies, etc.):
Project is a Cooperative Agreement funded by the USEPA, Water Engineering Research Laboratory, Drinking Water Research Division, Cincinnati, OH 45268 EPA/WERL/DWRD Project Officer is J. Keith Carswell, (513)569-7389.

Data reported above are considered preliminary and subject to revision.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

UPDATE ON SELECTED AWWARF ACTIVITIES

Health Effects/Toxicological Research

In 1987, the Research Foundation took its first steps into health effects research by sponsoring some evaluative studies. The primary purpose of this initial effort is to provide the water industry with basic information and understanding of the regulatory development process. The areas under study include a review of the health effects basis of federal drinking water regulations, specifically lead, trihalomethanes, and disinfection by-products. The purpose of this review is to examine the toxicological basis for certain regulatory decisions to ensure that the best scientific judgment has been used in making decisions. The contract to conduct these studies was awarded to Dr. Robert Golden, Karch and Associates, Washington, D.C., and initial results on the lead study are expected June 1988.

Program activities in toxicological research will be refined and modified as the Research Foundation becomes more sensitized to the needs of the water industry and gains a better appreciation of the intricacies of toxicological research.

Comprehensive Assessments - Definition of Research Needs

In 1987, the Research Foundation initiated a series of studies called comprehensive assessments to be used as a planning tool by the Foundation in the development of future research goals and projects. The project involves the selection of a number of topical areas and researchers to develop state-of-the-art reports, identify research gaps, and determine research needs in each area. From a lengthy list of potential topics, the following six were selected for study: Biological Treatment; Ozone; External Corrosion; Systems Control; Microbial Contaminants; and Radiochemicals. Principal investigators were selected because of their acknowledged expertise in the selected area. Three assessments have been completed (Biological Treatment, External Corrosion, and Radiochemicals) and executive summaries are included in this workbook.

In 1988, additional assessments will be conducted in the following areas: Oxidation, GAC Adsorption, Membrane Processes, Disinfection By-Products, Water Reuse, and Polymer Use in Water Treatment.

Assessment of Biological Processes in Drinking Water Treatment

Prepared by

Edward J. Bouwer
Assistant Professor
The Johns Hopkins University
Geography and Environmental Engineering
Baltimore, Maryland

EXECUTIVE SUMMARY

This literature review was conducted to obtain a better understanding of the application of biological processes in drinking water treatment and to identify needed research. Biological processes offer the potential to remove pollutants of concern, such as biodegradable organics, synthetic organic compounds, ammonia, nitrate, iron, and manganese, that may not be effectively removed by conventional water treatment practice. The oxidation of organic matter and ammonia through biodegradation would minimize microbial regrowth in the distribution system, reduce taste and odors, and decrease the amount of precursor available to react with chlorine and form halogenated organics. Removal of certain contaminants biologically could extend the service time or capacity of subsequent physicochemical processes. The practice in U.S. water treatment is often to preclude development of biological activity by prechlorination, rigorous scouring of filter media, and frequent regeneration of granular activated carbon (GAC). Practical experience with media containing microbial activity in Europe has been favorable and cost-effective, however, biodegradation in these engineered processes was often not the main objective and was not optimized. Consideration of biological process fundamentals and further research should lead to better performance.

Laboratory studies have demonstrated that bacteria can grow on the low concentrations of organic matter present in drinking water, and these oligotrophs have the potential to achieve very low effluent concentrations of biodegradable organic matter. The use of biofilm reactors is advantageous for drinking water. Accumulation of microorganisms as biofilms offers a reliable means to retain the organisms within the reactor and maintain a long biomass retention time. Relatively small process volumes are possible by the combination of high biomass retention time with low liquid detention time. Trace contaminants can be utilized by bacteria supported with higher concentrations of another substrate. Organic micropollutants, such as phenol, chlorinated benzenes, and halogenated aliphatics, were effectively removed in laboratory-scale biofilms by this process of secondary utilization. Microbial growth occurred through utilization of natural organic material or acetate supplement (1 mg/L).

Practical experience with TOC removal in pilot and full-scale drinking water treatment processes is with reactors of the biofilm type that include biological filters, fluidized beds, microbially active GAC, and ground passage. Significant reductions in total organic carbon (TOC) have been achieved over a long period of time. Removal of many chlorinated benzenes and aromatic hydrocarbons at trace concentrations occurred during dune infiltration, soil aquifer treatment, and in an expended GAC column. The combination of biodegradation and adsorption in the latter system is advantageous to increase stability and reliability throughout variations in operating conditions. GAC with microbial activity is also a feasible approach to retrofit a biological process into a conventional facility.

Ammonia in drinking water serves as a substrate to promote regrowth, combines with chlorine to form chloramines, and is a source of taste and odors. Nitrification processes have excellent potential to remove ammonia. A long biomass retention time must be maintained to achieve low ammonia levels. Successful removal of ammonia occurred in European plants using reactors with high specific surface area. Nearly complete nitrification of ammonia was observed in fluidized-bed biofilm reactors. The superior performance of the fluidized bed is achieved through the even distribution of the biofilm throughout the reactor while the liquid regime has plug-flow characteristics. A system that combines nitrification with heterotrophic oxidation of organics also appears advantageous. Laboratory research has demonstrated that organic products formed by metabolism of nitrifiers can serve as primary substrate for aerobic heterotrophs. Several trace organic compounds were utilized by the heterotrophs.

Nitrate contamination is becoming a frequent problem in agricultural regions. Addition of a carbon source to stimulate denitrification is a possible method to remove nitrate. Laboratory and full-scale fluidized-bed reactors have achieved a high degree of nitrate removal. The French have reported success with a denitrification filter using ethanol as the carbon source. Post treatment consisted of sand filtration, contact with GAC, and disinfection. In-situ nitrate removal by denitrification in groundwater holds promise so that above-ground treatment is not required. Hydrogen gas, hydrogen sulfide, elemental sulfur, thiosulfate, and sulfite are currently being examined as possible electron donors for reduction of nitrate utilizing innovative approaches involving autotrophic denitrification.

Iron and manganese are an aesthetic concern in drinking water and serve as electron donors for aerobic bacteria. Microbial oxidation of iron and manganese to insoluble forms is an alternative to chemical oxidation or aeration used in conventional treatment. Reductions in iron and manganese attributed to microbial activity were observed in rapid and slow sand filters, a fluidized-bed reactor designed for nitrification, GAC columns, and ground passage.

The performance and reliability of biological processes and their ability to produce safe water are major concerns. Application of basic concepts can improve reliability and performance and frequent monitoring is essential for maintenance of product water quality. Knowledge of the health effects of microbial products formed in biological processes and their impact on post treatment processes is presently inadequate. Excess carbon source in denitrification would increase TOC levels. Nitrite accumulation in nitrogen removal processes is also undesirable. Biological processes also release microorganisms through sloughing and erosion of attached biomass that may influence disinfectant demand and serve as an inoculum in distribution systems. Evidence suggests the released bacteria are generally non-pathogenic.

Biological processes should be one of the first unit operations in drinking water

treatment and be followed by a series of physicochemical processes. This increases reliability and provides multiple barriers to remove microorganisms, microbial products, and nitrite that may be produced. Further research is important to provide improved knowledge of the suitability of biological processes in drinking water. Some of these research needs include:

--The performance of fluidized-bed, sand filtration, ground passage, submerged fixed-bed, and microbially active GAC reactors for TOC removal, nitrification, denitrification, and iron and manganese removal at low concentrations characteristic of drinking water needs to be optimized.

--Simple reactors, ways to retrofit existing treatment plants, and innovative treatment technologies, such as autotrophic denitrification, in-situ treatment for contaminated groundwaters, systems with combined adsorption and biodegradation, systems with heterotrophs and nitrifiers, and systems with nitrification and iron and manganese oxidation need to be developed.

--Research efforts are needed to determine the kinds of contaminants in drinking water amenable to biological treatment, the kinetics of oligotrophic processes, and the environmental conditions required.

--A better understanding of the carbon source and dose for denitrification, kinetics of nitrate removal, and factors controlling nitrite accumulation is needed.

--Further characterization of substrate and nutrient concentrations that promote regrowth in distribution systems, the ability of biofilm reactors to remove these substances, and the impact of organic materials with slow biodegradation rates that pass through biological treatment on regrowth is needed.

--Research to determine factors controlling formation of microbial products, characteristics of the material (biodegradability, adsorbability, etc.), the impact on subsequent unit operations, reactivity with chlorine and other disinfectants, the need for post-treatment, and potential health effects of this material is desirable.

--Studies are needed to characterize the importance of bacteria released from biological processes, their impact on disinfection, and their potential as an inoculum in distribution systems.

WESTON

EXTERNAL CORROSION IN WATER DISTRIBUTION SYSTEMS
ASSESSMENT OF RESEARCH NEEDS

Prepared by:

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EXECUTIVE SUMMARY

INTRODUCTION

Corrosion has been estimated to cost approximately $180 billion in 1986. It has been further estimated that approximately $70 billion of this loss could be saved by the application of known corrosion control technology. These estimates include all metallic structures, not just underground water facilities.

Corrosion control of underground pipelines has a long history which some investigators have dated to over 4,500 years ago. Corrosion control engineering in a modern sense started in the early 1900s with efforts to protect buried gas and water lines. A major study was conducted by the National Bureau of Standards starting in 1910 to investigate the causes of stray electric current corrosion and the problems this was presenting to water utilities in the early 1900s. These problems were caused by the introduction of electrified transit systems.

It was not until the early 1920s that the Bureau concluded that serious corrosion occurred on underground structures not subjected to stray currents. Further research was initiated in the '20s to understand the causes of underground corrosion. Cathodic protection for underground pipelines was first reported in the United States in 1928. The development of the corrosion protection practice increased during the '30s and early '40s with the formation of the National Association of Corrosion Engineers in 1943. The National Bureau of Standards first published results of their underground corrosion research in 1945. In 1967, the Cast Iron Pipe Research Association (now Ductile Pipe Research Association) developed a soil corrosivity rating method for cast iron and ductile iron pipe.

The history of corrosion engineering is important because the understanding of the causes and controls for corrosion were developing during the period that many utilities in the United States installed hundreds of thousands of miles of gray cast iron and steel and later ductile water mains. Many of these lines were designed without corrosion control because the understanding of corrosion was limited.

CORROSION AND WATER MAIN DETERIORATION

There is a mixed set of opinions in the literature concerning the role of corrosion in water main deterioration. On the one hand, corrosion engineers often conclude that corrosion is the primary cause of water main breaks. This corrosion causes a weakening of

the pipe wall which results in ultimate leakage or failure. The other view is that corrosion is not a particularly serious problem and that only a small proportion of soils in the United States can be rated as highly corrosive. It is likely that corrosion is more serious than viewed by many investigators and is possibly less critical than viewed by some corrosion engineers. After review of the literature and interviews with water utility representatives, it is the author's judgment that corrosion problems are more serious than recognized by many water utility engineers and that improvements need to be made in controlling corrosion of water distribution systems.

The Philadelphia Water Department, the Boston Water and Sewer Commission, the Washington Suburban Sanitary Commission, and others have begun corrosion measurement programs to collect samples of water mains and to measure the depth of corrosion. Results to date indicate that many pipe walls have lost anywhere from zero to 40 percent of their wall thickness over the life of the main. There are significant variations in the extent of corrosion which are attributable to differences in soil conditions, design practices, and other factors.

REPORT OVERVIEW

This report has addressed the literature that is available on external corrosion and has presented an assessment of research into underground corrosion. Based upon this review, a proposed external research agenda has been prepared.

External Corrosion - The Basics

There are two primary types of corrosion in water distribution: galvanic corrosion and electrolytic corrosion. Both forms of corrosion include the flow of direct electrical current within a corrosion cell; the distinction is in the source of the current. Galvanic corrosion involves direct current which is self-generated within the cell, while electrolytic corrosion involves the flow of an externally generated direct current through the cell.

Galvanic Corrosion

Galvanic corrosion in a water distribution system includes corrosion which can result from the connection of two distinct materials such as a copper service line to a gray cast iron main. These dissimilar metals will generate a galvanic corrosion cell which will cause metal loss at the cast iron main. Galvanic corrosion cells can also be developed on a uniform pipe material

when there are differences in soil characteristics surrounding the pipe. As an example, differences in oxygen concentration between the top of the pipe and the bottom of the pipe can cause a galvanic corrosion cell which will generate a loss of metal on the main.

Electrolytic Corrosion

Electrolytic corrosion can occur when a DC current is impressed onto a main. The corrosion will occur at the location where the current leaves the main and returns back to its original circuit. Sources of stray DC current to water utilities include migration of current from a transit system as well as the interference which can be caused when other utilities have cathodic systems to protect their mains. This interference can cause the migration of DC current onto a water main and eventual corrosion of the water main where the current returns back to the original cathodic protection system.

EVALUATING SOIL CORROSIVITY CONDITIONS

Soil plays an important role in galvanic corrosion. The three roles include:

1. The soil can provide electrochemical differences which develop a galvanic corrosion cell.

2. Soil properties control the rate of corrosion.

3. Soil properties control the duration of corrosion and eventual depth of corrosion.

The technical literature shows that soil corrosivity is relatively well understood. The principal measures of potential soil corrosivity include soil resistivity, pH, sulfide, oxidation redox potential, and soil moisture. The water industry has been able to develop procedures to classify soils as to their potential corrosivity rating.

There has been limited progress in developing predictive capabilities to estimate the extent and severity of corrosion which is likely to occur based upon various soil conditions. At this time soil corrosivity can be qualitatively rated as more or less likely to cause corrosion. The inability to predict the depth and extent of corrosion limits our ability to evaluate the economic trade-off between alternative corrosion control techniques and our inability to assess the merits of these alternatives. Investigators have been able to quantify the life

expectancy of a pipeline to its failure based upon soil characteristics; however considerably more work is needed in this area to ensure that we have a reliable method for predicting the life of a water main.

CORROSION CONTROL RESEARCH NEEDS

In developing a corrosion control research agenda, there are two key issues which should be recognized by the Research Foundation namely:

1. Water utilities need to improve methods of corrosion control for existing buried mains. This is desirable so that the utilities can prolong the life of existing facilities to the maximum extent economically practical.

2. Water utilities need to develop improved methods of evaluating soil conditions and economic trade-offs of alternative corrosion control programs.

Two water utility corrosion control programs have been briefly reviewed to document the success that these utilities have had in implementing corrosion control programs. In both cases, the benefit/cost ratio for implementing corrosion control programs was significant.

The author found that many utilities have either no corrosion control program or a very minor corrosion control program. This is unfortunate because external corrosion is a significant problem in many cases. A series of research projects are proposed to improve water utilities' capabilities for maintaining existing water systems and for designing and building new systems.

EXECUTIVE SUMMARY

ASSESSMENT OF RECENT AND CURRENT RESEARCH ON RADIONUCLIDES IN DRINKING WATER

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October 1987

AWWA Contract No. 234(2)-87

This assessment of recent and current research summarizes the findings of work performed by Lowry Engineering. The effort was made with the help of Sylvia B. Lowry, Environmental Engineer, and a graduate student at the University of Maine, Michael Gray. In addition, numerous professional colleagues offered information and advice to make the report as complete as possible. The project was sponsored by the AWWA Research Foundation.

The objective of the assessment is to identify research needs based upon the most recent and current data available. To make the report more complete, background information is provided to support the more recent and current information. The following is a summary of the topics described in the complete report.

SECTION 1: Background

The concern for radionuclides in drinking water has increased dramatically in recent years as the media has covered the issue of radon in the indoor air of homes. It has also risen as a result of current activity by the EPA in preparation for the setting of new MCL's for the radionuclides.

This section provides background information about: 1) radiation physics; 2) naturally occurring and man-made radionuclides; 3) associated health concerns; 4) technologies for removing radionuclides from drinking water; and 5) existing regulations.

SECTION 2: Listing of Recent and Current Research

Twenty research and/or demonstration projects are identified in this section. The project title, sponsor, objectives, status, and findings are given where applicable. The projects range from those documenting the occurrence in

drinking water to ones dealing with the implications and problems associated with disposal and discharge of removed radionuclides. The projects are sponsored by private companies, water utilities, and state and federal agencies.

SECTION 3: Assessment of Recent and Current Research

The areas of: 1) Occurrence; 2) Impact; 3) Treatment Processes; and 4) Disposal are discussed in this section, as they pertain to the assessment of the recent and current research on radionuclides in drinking water.

The latest occurrence data clearly indicate that the real issue of radionuclides in drinking water is centered on the very small public, the non-community non-transient, and the private household ground water supplies. With few exceptions, there is less exposure in the larger ground water and in the surface water supplies.

Radon-222 is expected to have the greatest impact on the water supply field; however, this impact is speculative at this time due to the unknown value for the future MCL. An analysis for various MCL levels is given for the most important radionuclides: Rn-222, Ra-226 and 228, and U.

Treatment technologies are available to effectively remove problem radionuclides from either small or large water supplies, and it appears that these processes are relatively economical. A few of these technologies are somewhat unique and are discussed in detail. These include GAC adsorption/decay, the radium complexer, high capacity anion exchange, and processes for radium removal designed to use existing conventional treatment plants.

The problems we face with radionuclide removal from drinking water appear to be the most challenging in the area of radiation buildup on resin, GAC, and in waste streams. In addition, the discharge of Rn-222 from stripping towers will likely cause concern in some states. This section identifies these potential problems and discusses their implications.

SECTION 4: Conclusions and Research Needs

The final section of the assessment identifies the needs for research, which address the areas of: 1) Occurrence; 2) Impact; 3) Treatment Processes; and 4) Disposal. In general, radionuclides in drinking water have received little attention as a result of few MCL's or limited enforcement of existing MCL's. Resources have been few and thinly spread among a number of topics that appear to need additional study. More documentation at existing treatment plants could provide needed information relatively quickly to the water utility field.

CONCLUSIONS AND RESEARCH NEEDS

This section details the conclusions and the related needs for research and investigation for radionuclides in drinking water. The information is based upon the material presented and analyzed in the preceding sections. It is also based upon many conversations and communications with professionals in the field who helped compile the information in this assessment. These individuals are listed in the Appendix.

CONCLUSIONS

1. The naturally occurring radionuclides of the ^{238}U decay series, namely ^{226}Ra, ^{222}Rn, and U are responsible for the overwhelming majority of the radiation exposure associated with drinking water. Ra-228 is also found at significant levels in some cases.

2. Rn-222 represents the most serious health risk for radionuclides in water, through its slight contribution to the indoor air ^{222}Rn levels in homes. As a result, it is anticipated that the upcoming MCL for ^{222}Rn will be relatively low at approximately 1000 pCi/L. This is in contrast to existing recommended levels of 10,000 to 20,000 pCi/L by some states.

3. It is clear that the most significant exposures to people from radioactivity in drinking water occurs in the very small public and in private water supplies, as opposed to public water supplies serving greater than a few hundred population. This is based upon the fact that the limited data available indicate that radionuclide problems are much more frequent and severe in low yield private ground water supplies.

4. While several investigations have focused upon the occurrence of radionuclides in public water supplies, very little effort has been directed at the significant portion of the population that gets its water from very small public and private water supplies. As a result we have little information on the real exposure and risk to this portion of the population.

5. Overall, the impact upon the water supply industry due to MCL

enforcement for radionuclides is expected to be small, with the possible exception of ^{222}Rn. If a very plausible low MCL is set for ^{222}Rn, a significant fraction of the existing ground water supplies will be in non-compliance.

6. Removal of radionuclides from water supplies is relatively simple, and economical processes are available for both large and small supplies.

7. While removal is relatively easy and economical, the disposal of removed radionuclides can represent a limiting factor in terms of feasibility and economics. Limited experience and familiarity with this is a major impediment; however, as information is more generally available to both the water supply field and regulators many of the problems raised will be more easily solved.

8. The most effective processes for the small public water supplies are somewhat unique in their application to U, Ra, and ^{222}Rn. Anion exchange and the radium complexer have extremely high capacities for U and Ra, respectively, and ^{222}Rn can be easily stripped by packed tower or other form of aeration. GAC exhibits an adsorption/decay phenomenon that allows it to be effective for an indefinite but very long time.

9. A new process involving sorption to HMO in existing treatment plants shows promise to solve Ra problems in the Midwest.

10. A somewhat negative finding has recently emerged from recent research on the removal ^{222}Rn with GAC. It appears that many of the isotopes of the ^{238}U decay series are well adsorbed to carbon, including U and Pb. This coupled with the relatively low levels allowed for U and ^{210}Pb on materials by some states means that many POE and public water supply applications of GAC probably could be classified as licensable. This is especially true for ^{210}Pb, since it would take only a short time to accumulate as a result of the adsorption/decay of even low ^{222}Rn levels in ground water. In fact, limited data indicate that many POE GAC beds and most GAC beds treating public ground water supplies are likely to contain more than the exempt

quantity of ^{210}Pb. This appears to be the case even for ^{222}Rn levels as low as 100 pCi/L in public water supplies. What the implications of this are is not known, since this is a very recent and largely undocumented finding.

11. Compounding the problem of disposal is the fact that few traditional water regulatory agencies are experienced with handling these materials. It appears that it will be up to the states to handle these problems, as the NRC does not regulate natural radionuclides and EPA has not yet come out with a document dealing with these problems.

RESEARCH NEEDS

The following proposed research projects address the gaps in current and recent research. The listing is not in order of priority.

Project No. 1 :
Survey of Natural Radionuclide Levels in Private and Non-Transient Non-Community Water Supplies. Po-210 should be included as required.

Objectives:
To document the levels of natural radionuclides in very small and private water supplies and to estimate the health risk associated with those levels.

Benefits:
Very limited information on the levels of natural radionuclides in very small and private water supplies exists. What little information there is supports the belief that the problem of radionuclides in water is largely one associated with small supplies that do not or have not come under the previous documentation efforts by EPA and others. Extreme levels are approximately an order of magnitude higher in these low yield wells, as compared to relatively well documented levels of ^{222}Rn, Ra, and U in public water supplies. Since a significant population obtains their drinking water from these supplies it is

important that the associated exposure be better documented. Burnett, et. al., (1987) indicated that ^{210}Po can be very high in well supplies and this point should be addressed.

Cost:

It is not expected that such an investigation could be carried out by one body and this type of project would be best conducted by the individual states. Therefore, a cost estimate is not given.

Project No. 2:

A General Assessment and Documentation of the Ability of Existing Treatment Facilities to Remove Radon From Water Supplies.

Objective:

To expand upon the type of limited information obtained by the recent study by the American Water Works Company (Phase II). Treatment efficiency of aeration, GAC, other processes, and losses in the distribution system should be documented for existing systems.

Benefits:

The excellent report by the American Water Works Company added much information for a relatively small investment. This effort represents some of the best data available on aeration and distribution system losses. An expanded study could produce some valuable data not generally available at the present time. A more thorough analysis of removal by existing treatment processes could provide a significant amount of data very quickly. Distribution system losses could be studied and possibly optimized through such a study.

Costs:

It is estimated that the cost would range between $25,000 and $35,000, with the lower figure representing an effort roughly twice that covered by Phase II of the previously referenced study.

Project No. 3:

A Study of U Removal By Anion Exchange and GAC.

Objectives:

To further document the following aspects of U removal:

1. the effect of pH on the removal of U by anion exchange columns
2. the effect of pH on the removal of U by GAC beds
3. the water quality and operating parameters that determine the resin capacity for U
4. the use of mixed resin beds to remove U and Ra from the same water supply
5. the fate of thorium-234 (^{234}Th) and protactinium-234 (^{234}Pa) in resin beds used to remove U from water.

Benefits:

Data are very limited on the effect of pH on U adsorption or exchange (Lee and Bondietti 1983). At pH 9.0 it has been shown that GAC does not adsorb U very well, yet at pH 6.8 it adsorbs and retains it very well. Also, there is evidence that pH is very important to U removal by anion resin, although no studies have investigated this to a significant degree. This part of the study would provide needed information on the extent that U is adsorbed by existing GAC beds and, therefore, provide an estimate of the potential for this to be a disposal issue.

While pH is probably very important to U removal with anion resin, it appears that other factors may also be important in determining capacity. Studies have documented that the capacity of the resins for U varied widely from about 10,000 bed volumes to over 100,000 bed volumes. This study would investigate the factors that produce such a wide variation.

In small supplies in some regions of the country U and Ra are both found at elevated concentration. In these cases a mixed bed with either anion/complexer or anion/cation could be used to remove both radionuclides in one vessel. This study could provide design information and investigate the possibility of a one time resin use and disposal without regeneration for the

complexer/anion mixed bed. Both these materials have extremely high capacities for the respective radionuclide and might prove to be a very useful combination in these cases.

The fate of the relatively short-lived progeny of U, ^{234}Th and ^{234}Pa, has not been studied. Since the capacity of the resin is so high for the U salt anion, these beds may be operated for an extended period such that the generation of these two progeny will become significant. This possibility and the fate of these isotopes should be investigated.

Costs:

It is estimated that the study described would cost between $50,000 and $100,000.

Project No. 4:

Documentation of the Occurrence of U and Ra in Wastewater and Water Sludge.

Objectives:

To gather further information about the U, and to a lesser extent Ra, content of waste sludge.

Benefits:

There is indication from the few measurements that have been taken that U levels in some sludges can be very high and that, in general, sludges concentrate U to a high degree. The documentation of the U content in sludges associated with waters containing some U would provide a perspective upon the ubiquity of U in the environment. A realization that U can be easily found in materials we are used to handling, may provide a benefit to those dealing with the question of waste disposal. The recent discovery in Colorado of a septic tank sludge containing U at over the licensable quantity specified by the NRC precipitated a decision by the State of Colorado to not consider this material as a low level radioactive waste. It is likely that the widespread occurrence of U in that area would cause a greatly increased regulatory demand if such a

practical decision were not made. Perhaps regulators in other states would view water treatment residues and discharges in a more practical way if they were aware of the widespread occurrence of concentrated U in these familiar materials. For example in New Hampshire, at the present time many of the GAC beds treating ground waters probably have in excess of the allowable quantity that differentiates between normal and low level radioactive waste, according to that state's office of radiation. In reality, it is unlikely that New Hampshire will have the resources to measure, let alone enforce, this criterion; however, it appears that a perspective on the water treatment field is needed.

Costs:

It is expected that a project would be best conducted by the individual states; however, the perceived questionable benefits and limited budgets will probably prohibit this. It is estimated that this survey could be done for $25,000 to $50,000, depending upon the scope. This might provide that between 200 and 400 individual samples be analyzed.

Project No. 5:

A Study of the Radioactivity of Existing GAC Beds Treating Ground Waters Used for Public and Private Supplies.

Objectives:

To document in the field the ability of GAC to adsorb the uranium series isotopes, including U, Rn, Po, Bi, and Pb, and to determine the extent of any disposal question that may be associated with these materials. The isotopic content of the GAC, its associated gamma exposure rate, and specifically its U and ^{210}Pb content should be measured.

Benefits:

Relatively recently Lowry documented that GAC effectively removes and concentrates most of the isotopes in the U decay series. This has prompted some regulators to take a look at GAC as a possible low level radioactive

waste — a direction that would have a tremendous impact upon the carbon industry and the water treatment field. Recently, the author and the EPA have calculated that the majority of the existing GAC beds that presently treat ground water could contain greater than the exempt quantity of ^{210}Pb, used by some states for licensing purposes. In fact, even a significant number of the small private POE units will contain greater than the exempt quantity, which is 100 nCi. This is true for GAC units in general use on ground water supplies, whether or not they were specifically intended to remove ^{222}Rn.

It is not yet clear what the implications will be when this becomes general knowledge; however, the extent of the potential problem needs to be identified so data will exist. Further, it is not clear to regulators involved in this area what the actual regulations should be with respect to the water field.

Costs:

It is expected that a study to document the extent of this problem would cost between $80,000 and $200,000, depending on the scope.

Project No. 6:

A Study of ^{222}Rn Adsorption From the Discharge Air of a Packed Tower Aeration Process.

Objectives:

To document the feasibility of ^{222}Rn removal from the air discharge of a stripping tower.

Benefits:

While packed tower aeration appears to be much more economical than GAC on a public water supply scale, there are states that require that the discharge from a packed tower air stripper be scrubbed with GAC. The feasibility of doing this has not been demonstrated and it is known that slight changes in humidity deteriorate the effectiveness of ^{222}Rn adsorption from the air. It may be that air scrubbing for ^{222}Rn is not economical, leaving GAC the only

available method for removal. This possibility should be investigated.

Costs:

It is estimated that this short-term study would utilize an existing stripping tower and would cost approximately $30,000 to $40,000.

Project No. 7:

Pilot and Full-Scale Demonstrations of Radionuclide Removal Technologies for Small Water Supplies.

Objectives:

To provide routine operation data for processes such as cation exchange, Ra complexing, HMO removal of Ra, anion exchange, and GAC adsorption/decay. These processes are somewhat unique in terms of their capacity, expected life, and the associated disposal considerations, and need to be better documented in the field.

Benefits:

Very limited data are available for the routine operation of anion exchange for U, Ra removal by the Dow complexer and HMO, and for GAC removal of ^{222}Rn. Anion resin capacity appears to be rather variable depending upon which study is referenced and little information is available on actual bed capacity for full scale operation. GAC is being studied by a demonstration project in New Hampshire; however, it appears that conditions possibly unique to that site are causing carbon fouling and yielding unrepresentative data for ^{222}Rn removal. More studies and demonstrations are needed upon which to base future design and operations.

Cost:

The cost for a series of studies could be quite substantial, depending upon the magnitude and scope of the effort. It is envisioned that studies of some of the first operational plants using these processes, some of which exist at present, could be coordinated with the water utilities or owners to provide

this documentation. It is estimated that a limited study of an existing process might be conducted for between $30,000 and $50,000 per process; however, this is a very approximate figure.

USSR

USSR

EMERGING WATER SUPPLY TECHNOLOGY AWWARF Code #: USSR-01

PROJECT DESCRIPTION

Project Title:

Water Quality of Moscow Water Supply Sources in Prognostications.

Contact (name of person, organization, address, telephone):

USSR, S.V. Khramenkov
Head of Main Administration for Water and Wastewater
Management of Moscow City Soviet (GLAVMOSVODOCANAL)
USSR 107005 Moscow, Pleteshkovsky per.,4
Phone 261 67 20

Project Description (Please attach a schematic diagram if appropriate):

Moscow water supply is based on two sources of water. The first source is the River Moskva with its tributaries and storage reservoir system. The second one is the River Volga and the water supply is performed via the Moskva-Volga Canal.

For the implementation of such an approach it is necessary to forecast the quality of water at every stage of the water supply system because of the complicated water source morphological structure of the Moscow water supply system (wide catchment area, water storages, channels, mains and pipelines and other hydraulic structures).

Prognostications are used to solve problems of water protection and modernization of water purification technology; seasonal and emergency forecasting is available for planning and management of the treatment process.

Water treatment control is conducted by means of variation of technological methods:

- using different kinds of chemicals;
- composing variable combinations of chemicals and changing the point for adding chemicals from time to time;
- changing water treatment regime (chemical dosage, filtration rate, settling time).

Operating and cost data (including data on efficiency, results, etc.):

A complex approach to the problem "water supply source - waterworks system" allows to plan both the water treatment mode at a waterworks and the chemical dosage with the sufficient lead time by forecasting water quantity in the water supply source.

Place(s) of installation/application (including dates):

Moscow water supply system.

Patent staus, if applicable:

None.

Other information (e.g., funding source, cooperating agencies, etc.):

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

WATER QUALITY OF MOSCOW
WATER SUPPLY SOURCES IN PROGNOSTICATIONS

S.V. Khranemkov, USSR

Moscow water supply is based on two sources of water. The first source is the River Moskva with its tributaries and storage reservoir system. The second source is the River Volga and the water supply is performed via the Moskva-Volga Canal. (Fig. 1)

Water supply sources have been developed gradually. Such water storages as Istrinskoye, Mozhaiskoye, Fuzskoye, Ozerninskoye with water resources enough for long-term flow regulation being built on the River Moskva and its tributaries provide for the output about 32 m3 per second in a dry year. With the construction of Vazuza Hydro-Engineering system we have got the possibility to cover completely feasible shortage of water in definite districts of the city.

The capacity of the Volga water source at present time has reached 82 m3 per second and that of the Vazuza system - 17 m3/sec.

The total design capacity of water sources was 131 m3 per second in 1987. It fully satisfied the city demand for water.

On an average day we supply totally 5.8 million cubic meters of water; the maximum water consumption totals 6.4 million cubic meters a day.

The purification of surface water and the supply of potable water to the consumer are facilitated at four waterworks: Rublyovskaya and West waterworks (water comes from the Moskva); East and North waterworks (water comes from the Volga).

Further development of city water supply is envisaged on the basis of these water sources.

In order to guarantee the quality of drinking water, it is vital to have the reliable purification technology designed for possible change of the quality of the water near intakes. The quality of the water at waterworks intake is the factor which determines the treatment regime. That is why when designing and constructing purification facilities is very important to have long-term information about the quality of the water. Taking into consideration substantial investments in construction and reconstruction of the treatment facilities is necessary to use complex approach to the problem "water supply source - water station system" that is the execution of the analysis of the alternate variants (different measures to secure the improvement of the water quality in the water source or modernization of treatment facilities) by means of comparison of their cost effectiveness.

For implementation of such an approach it is necessary to forecast the quality of water at every stage of the water supply system because of the complicated water source morphological structure of the Moscow water supply system (wide catchment area, water storages, channels, mains and pipelines

and other hydraulic structures). Forecasting of the water quality at every stage on the way to intakes of waterworks is performed at both water supply sources. Prognostications are used to solve problems of water protection and modernization of water purification technology; seasonal and emergency forecasting is available for planning and management of the treatment process.

Water treatment control is conducted by means of variation of technological methods:

- using different kinds of chemicals;

- composing variable combinations of chemicals and changing the point for adding chemicals from time to time;

- changing water treatment regime (chemical dosage, filtration rate, settling time).

The necessity to make these evolutions is caused by fluctuations of the quality of surface water at the waterworks intakes. The change of the water quality is evaluated with the help of meteorlogical, hydrological and anthropogenic factors.

Furthermore, the change of water quality also arises from the alteration of the conditions of the water objects, increase of the water intake from the water storage when the water consumption in the city is growing.

In Fig. 2 and 3 are shown typical curves of twelve months' and several years' standing changes of some indices of the water quality in the Volga and Moskva water supply sources. Data analysis presented in these pictures shows what for Moscow water supply sources on the background of tendency for relatively slow change of the conditions of water objects are characteristic considerable fluctuations in the water quality indices recorded at the waterworks intakes.

Meanwhile adopted in the USSR drinking water standard (GOST 2874-73) standardizes upper and lower limits of the quality indices in rather narrow range irrespective of the value of water quality fluctuations in the waterworks intakes. Fig. 4 demonstrates limiting values of standard demands to drinking water quality. Under existing conditions the technology of water treatment can guarantee standard quality of drinking water only when treatment facilities are operated on the principle of flexible technology which is characterized by dominating demand to regard the dynamics of water supply source. Water supply source dynamics is characterized by three basic processes:

- water quality change when there is natural transformation of water body as a result of the accumulation of different changes caused by natural and anthropogenic factors;

- twelve months' changes periodically repeated with various intensity in different years depending on total phenological background;

- water quality caused by short-term fluctuations of environment in case of emergency.

Timely taken mentioned processes into account allow to utilize all stages of the flexible technology that is to choose the right water treatment technology and optimal treatment regime. It is very important to foresee the long-term prospective tendencies of changes of water quality indices when estimating the technology of water treatment process.

This information is used when carrying out projecting and research work on finding the most rational technological methods of water purification in order to meet standard demand for water quality.

The reliability of various schemes of water treatment is solved by means of forecasting the quality of the water for the planning period.

At last, it is very important to have information about the water quality when choosing rational treatment regime. The period for forecasting the quality of the water should be composed, as minimum, of time necessary to make calculation of a treatment regime and time which is necessary to change the operation of treatment facilities to a new operational regime.

In such a way, on the basis of execution of an effective water treatment control is a great need in long-term, middle-term and short-term forecasting of the water composition in the water storage reservoir.

For example, when choosing prospective water treatment technology at waterworks using water from the storage reservoir which belongs to the Volga water supply source, that is, East waterworks, long-term forecasting of the water quality in the reservoir was developed. Forecasting was made on the basis of analysis of the results of many years' standing observations which were started in 1937 immediately after the construction of the water storage reservoir was completed.

The analysis of statistic data showed that with the increase of water intake reached in 1987 about 3.5 mln cubic meters a day (versus 0.4 mln cubic meters daily in 1937) the protection function of the water storage reservoir decreased with respect to especially color index. In Fig. 5 (curve 1) is shown that the color index at the water storage inlet fluctuates within the limits from 30 to 90 degrees. For all that as a result of self-purification, the value of this index decreased (curve 2). The distance between the two curves shows the cleaning effect of the water storage.

Fig. 6 demonstrates the diagram plotted according to the results of observations. It shows the decrease of water color index in water reservoir with the growth of water demand for the whole period of its service life. It is accepted that the ratio between the difference of the color index at the water storage inlet C_1 and in the waterworks intake C_2 to the value of C_1 to be as the cleaning effect index of the water storage. For the analysis were used average annual values C_1 and C_2.

Judging by prognostications was made a conclusion that it would be impossible to meet the quality standards for drinking water during some seasons of the year when using only conventional two-stage treatment scheme "sedimentation-filtration." As the result of many experimental studies was taken the decision to improve the structure of the treatment process by means of introduction of additional treatment stage - ozonation.

More than 10 years of service life of ozonation station proved correctness of these long-term prognostications and of the chosen technology of the purification process. At present time and for future the technological process of water purification at East waterworks includes sedimentation-filtration with the application of chemicals-chlorine, ozone, aluminum sulphate, ammonium, lime and from time to time, activated carbon.

Depending on the quality of raw water the possibility of choice of the most rational treatment regime is provided.

In warm seasons of the year when the water temperature is more than 10°C and coagulation processes proceed actively two-stage purification scheme is capable to meet standard demand for drinking water without the ozone application.

On the contrary, at low watei temperature ozonation is more effective - filtration process takes place without the addition of coagulating agent and sedimentation, as well as chlorine dosage for primary chlorination and lime dosage are reduced.

Because of the unstable chemical consumption it is necessary not only to determine its total volume but also to work out the time table for delivery of chemicals. Regarding considerable volumes of chemical consumption (it is used up to 10 thousand tonnes of coagulating agent only at one of the Volga supply source annually) the solution of this problem has a great economic importance.

To forecast the delivery of chemicals for the period of one year, to form its stock with view of having reserve enough for the application of any existing purification schemes we use the water quality forecasting with lead time of 1.5 years.

The water quality forecasting for such period of time is performed by one of the widespread prognostication methods, that is, the analogue method. The whole point of the analogue method is that out of stored water quality data is done search of annual change of quality data which is very close by its trajectory to the water quality of the running year which is assumed as the basic one. The search of analog is executed with the help of methods of mathematical statistics; water quality trajectory following the found analog of basic year is taken as a forecasting trajectory.

Data analysis of forecasting secures planning of chemical costs with the error admissible for water treatment technology. In Fig. 7 are demonstrated forecasting errors of average month values of color index, received by means of comparision of prognostication data with actual values. Color forecasting error makes up to 8-13%. There are some other results of water quality indices in this table. All together nine the more important quality water indices are included into this system.

Existing system for delivery of chemicals during a year allows to make quarter period correction of planned chemical quantity. To determine the necessity for such correction is created quarter forecasting of the water quality with the 3 months lead time. Such prognostications are carried out

at the end of each quarter according to analogue method, too. Results of water quality forecasting are presented in table 8. Comparison of forecasting errors shows the degree of forecasting accurate definition when lead time period is reduced.

The storing of data file, further filing of the information, calculation of annual and quarter prognostications of the quality of the water are performed with the help of a computer in automatic mode on the basis of the water quality initial data.

In Fig. 9 retrospectively is shown forecasted and actual annual chemical consumption (chlorine and coagulant). It is possible to decrease chemical stock using forecast information about the water quality. For example, prognostications of the chemical consumption proved the possibility of the reduction of the coagulant stock by 25-30% at East waterworks. Advisable stock of coagulant (including emergency store) makes 2500-3000 tonnes. Thus, medium-term forecast of water quality ensures availability of chemicals delivery initial information for plan calculation and estimation of chemical stock volume.

Even very well organized safety system couldn't protect the water source from uncontrolled accidental occurrences. As know, accidental occurrences are unamenable to long-term and medium-term forecasting. For this purpose short-term forecast system is available.

It is mentioned in the list of comments of results of different water quality factors forecasting of the water supply source that analogue method of forecasting provides various values of errors for different kinds of components. The example of the analysis of forecasting error of ammonia concentration which content in the water serves as one of the factors of anthropogenic effect influencing the quality of water object (error is 80%), shows that forecasting calculating methods for some quality indices can't be reckoned to be satisfactory.

Though, in response to the length of water course, water circulation character and self-purification processes, we are capable to forecast the influence of accidental deterioration of the water quality at the waterworks intake.

Many years of exploitation of Moscow water supply sources proved that the major method of short-term forecast is the monitoring of water quality indices in the control sections of the river and canal remote from the waterworks intake for a distance enough to make changes in the technological scheme and to use another treatment process regarding transportation time and possible transformation of pollutants.

To secure forecasting accuracy is foreseen the possibility of dubbing the water quality monitoring in different control sections. So in the Moskva and Volga water supply sources, the sytem of control points includes from 5 to 15 control sections which measure up to 10 various water indices which determine the treatment process at the waterworks. There are automatic control stations at some control sections as well as mobile ones to get express information about movement of pollution front along watercourse to

the intake. Such monitoring system provides prognostications of the quality of the water for the period up to 30 days. At this, quite evident, that the sooner water quality information will be given to operating staff, the higher level of adequate treatment mode will be chosen. Necessary time reserve is provided by short time forecast. Express method of water treatment regime calculation is carried out by personal computer installed at the disposal of an operator of waterworks. Calculations are made with the help of the mathematical model of purification facilities.

This model was worked out to control the process of purification. Mathematical model of the waterworks represents the whole combination of analytical dependences uniting into common system water quality indices recorded in the intake of the treatment facilities, doses of applied chemicals and the quality of the purified water.

With the help of these dependences different combinations of chemical dosages are calculated and other purifying effects which secure the required water quality standard are estimated, too.

Out of set of combinations the regime is calculated which can provide the most rational mode of the treatment process. In particular, this calculating program is expected to choose such purification mode which would have minimum cost price.

Besides the water quality index in the waterworks intake, such factors as the capacity of treatment facilities and their technical conditions (number of settling tanks, filters, contact basins, etc.) are considered to be the factors also determining the purification regime.

In table 12 are presented the results of calculation of the working regime of the treatment facilities during one of the days each month of the year.

Thus, the calculation of purification regime and optimal consumption of chemicals performed with the help of computerized control board installed at the disposal of an engineer on technology permits to increase the reliability of the facilities to treat water to forecasted quality.

AWWARF Code #: USSR-02

EMERGING WATER SUPPLY TECHNOLOGY

PROJECT DESCRIPTION

Project Title:

Artificial Underground Water Fill Up Using Direct Filtration.

Contact (name of person, organization, address, telephone):

Skirkiavichus A.L.
Ministry of the Municipal Services of the Lithuanian SSR
4 K.Didjulio St.
Vilnius, 232753 USSR
Tel 622-875

Project Description (Please attach a schematic diagram if appropriate):

River water clarified by fast filters is processed to infiltration reservoirs having the total area of 50,000 m^2. The operational depth of the reservoirs total 2.7 m. Wells drilled in the reservoirs' area draw up to 45% of the infiltrated water. Water probes from reservoirs and control wells are taken to examine the infiltration regime. Water lowering speed after water supply to the reservoirs is stopped is also measured.

Operating and cost data (including data on efficiency, results, etc.):

The total water intake debit after commission of the artificial water fill up system has been increased by 1.4 times, reaching an average daily debit of 35,000m^3. The underground water level in the reservoirs' area has registered an average increase of 1.5 meters.

Place(s) of installation/application (including dates):

The Aguliaisk water intake, the city of Kaunas. 1975

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

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The Aguliaisk water intake, the city of Kaunas. 1975

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

EMERGING WATER SUPPLY TECHNOLOGY

AWWARF Code #: USSR-03

PROJECT DESCRIPTION

Project Title:

Artificial Underground Water Fill Up Using Side Filtration

Contact (name of person, organization, address, telephone):

Skirkiavichus A.L.
Ministry of Municipal Services of the Lithuanian SSR
4 K.Didjulio St., Vilnius 232753 USSR
Tel 622-875

Project Description (Please attach a schematic diagram if appropriate):

The pumping station supplies water from the old navigation canal to the system of filtration canals along which wells are drilled (H=20.0m) or drains are installed (H=8.0m ø 600mm). The canal is 2.5m deep with the bed width of 1.5m and the upper width reaching 15m. Water turbidity in the main canal doesn't exceed 15mg/l. Water intake facilities process up to 60% of the infiltrated discharge. Once or twice a year infiltration canals are washed using excessive washwater.

Operating and cost data (including data on efficiency, results, etc.):

This method helped to convert polluted surface water into underground potable water without complex and expensive treatment in the area that has no potable water sources.

Place(s) of installation/application (including dates):

The facilities were installed at the Klaipeda water intake and the canal connecting the Miniya and Kurshsk Bay in 1975.

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

EMERGING WATER SUPPLY TECHNOLOGY AWWARF Code #: USSR-04

PROJECT DESCRIPTION

Project Title:

Artificial Underground Water Fill Up Using Well Filtration

Contact (name of person, organization, address, telephone):

Skirkiavichus A.L.
Ministry of the Municipal Services of the Lithuanian SSR
4 K.Didjulio St., Vilnius
232753 USSR
Tel 622875

Project Description (Please attach a schematic diagram if appropriate):

Chlorinated river water processed through speed filters is supplied to the wells. The second line of aprallel wells is used for further water intake. The number of wells in a line totals 10 (each 80m deep). River water turbidity ranges from 2 to 250 mg/l. That is why it is taken only dry, clean periods with the water turbidity not exceeding 10-15 mg/l (not more than 100 days a year). It has been proved that the turbidity of the infiltration water should not exceed 5 mg/l. The take in of the infiltration water equals 50%.

Operating and cost data (including data on efficiency, results, etc.):

This method of underground water fill up ensures a three time increase in the intake capacity. (from 4,500 m^3 to 15,000 m^3 daily).

Place(s) of installation/application (including dates):

Facilities were installed at the Tauragsk water intake in 1978.

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

PROJECT DESCRIPTION

Project Title:

Dry Beam Water Intake

Contact (name of person, organization, address, telephone):

Skirkiavichus A.L.
Ministry of the Municipal Services of the Lithuanian SSR
4 K.Didjulio St. Vilniu 232753
Tel 622-875

Project Description (Please attach a schematic diagram if appropriate):

A beam underbed water intake used in areas with favourable hydrogeological conditions has proved to be a cheap and effective way of water intake. The well of the Kaunas beam water intake has the depth of 28.0 m and the diameter of 6.0 m, 17 ø150 mm drains with staggered 1 + 2 x 10 + 12 mm lazer cut holes. The well is dry. Drains are grouped into 7 sets with 2-5 drains in each set. Deep water pumps are installed in metal pump columns. Such composition ensures free manoeuvre of drains' operation and maintenance.

Operating and cost data (including data on efficiency, results, etc.):

The dry beam water intake is 5 times cheaper than the well intake of similar capacity.

Place(s) of installation/application (including dates):

The beam well with a daily capacity of $30,000m^3$ is installed at the Vichiunay water intake, Kaunas, USSR.

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

EMERGING WATER SUPPLY TECHNOLOGY

AWWARF Code #: USSR-06

PROJECT DESCRIPTION

Project Title:

Well Restoration Complex

Contact (name of person, organization, address, telephone):

Skirkiavichus A.L.
Ministry of the Municipal Services of the Lithuanian SSR
4 K.Didjulio St., Vilius 232753 USSR
Tel 622875

Project Description (Please attach a schematic diagram if appropriate):

A complex of units mounted on two trucks is used to restore operational capacities of well filters. The complex comprises an electrical-hydraulic plant, a living section and a depot for auxilliary equipment mounted on the one truck and a pumping and acidification units mounted on the other. There are two tanks with acid, compressor and a winch for maintenance of the air lift device. The complex is run by a 5 man team. Maximum immersion of liquid discharger is 100 m. It takes one week to restore one well.

Operating and cost data (including data on efficiency, results, etc.):

The restored operational capacity of three wells saves the construction of one new well.

Place(s) of installation/application (including dates):

The complex is produced by start-up and adjustment workshops, the Department of the Republican production amalgamation of the water supply and sewerage facilities, Ministry of Municipal Services. In operation since 1985.

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

EMERGING WATER SUPPLY TECHNOLOGY AWWARF Code #: USSR-07

PROJECT DESCRIPTION

Project Title:

Mobile Chlorination Unit

Contact (name of person, organization, address, telephone):

Skirkiavichus A.L.
Ministry of the Municipal Services of the Lithuanian SSR
4 K.Didjulio St. Vinius 232753
USSR Tel 622875

Project Description (Please attach a schematic diagram if appropriate):

In the Republic with small water supply systems there are no reservoirs no second lift pumping stations or stationary chlorination facilities. Mobile chlorination units produced in our Republic are widely used to chlorinate the water supply net and reservoirs after repair and for preventive purposes. These units have independent power supply and can be connected to the mains. The trailer mounted chlorination unit consists of three sections: a tank with chlorine, equipment sector and the operator's section. The tank with chlorine is covered by a steel casing jacket to ensure labour safety conditions. The output of the unit is 1.5 kg/h. The water pressure in the chlorinated water supply net should not exceed 6 atm. Chlorine consumption: 1 tank per 44 km pipe (ø 200 mm) or 19 km line (ø 300mm), or 7km line (ø 500mm) or 1350 m^3 reservoir. The minimum outside temperature is -30°C.

Operating and cost data (including data on efficiency, results, etc.):

Timely chlorination using mobile units ensures desired sanitary conditions of the water supply system in small towns and saves the costs of construction of expensive stationary facilities.

Place(s) of installation/application (including dates):

The mobile chlorination unit is manufactured at the start-up and adjustment workshops, the Department of the Republican production amalgamation of the water supply and sewerage facilities, Ministry of Municipal Services. In operation since 1984.

Patent staus, if applicable:

Other information (e.g., funding source, cooperating agencies, etc.):

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

WEST GERMANY

WEST GERMANY

EMERGING WATER SUPPLY TECHNOLOGY AWWARF Code #: WG-01

PROJECT DESCRIPTION

Project Title:

Combined hardness and sulphate/nitrate removal by the CARIX ion exchange process

Contact (name of person, organization, address, telephone):

Dr.-Ing. habil. Wolfgang H. Hoell

Karlsruhe Nuclear Research Center, Institute for Radiochemistry
Water Technology Division
P.O. Box 3640
D-7500 Karlsruhe (F.R.G.)

Project Description (Please attach a schematic diagram if appropriate):

See attached literature

Operating and cost data (including data on efficiency, results, etc.):

Place(s) of installation/application (including dates):

Patent staus, if applicable:

Europ. Pat. No. 0056850, US Pat. No. 4,448,693

Jap. Pat. No. 10810, Can. Pat. No. 1,186,075

Aust. Pat. No. 86723

Other information (e.g., funding source, cooperating agencies, etc.):

See Display Material to be available at Conference.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

Wat. Supply, Vol. 6, Brussels. pp. 51–55, 1988.
Pergamon Journals Ltd. Printed in Great Britain.

0735–1917/88 $0.00 + .50

COMBINED NITRATE AND HARDNESS ELIMINATION BY THE CARIX ION EXCHANGE PROCESS

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ABSTRACT

The combined application of a weak-acid ion exchange resin in the free-acid form and of an anion exchanger in the bicarbonate form allows a combined elimination of nitrate, sulfate, calcium and magnesium from drinking water. The process uses CO_2 for the simultaneous regeneration of both resins. As a consequence, the effluent contains only the amount of salt which has been eliminated in the service cycle. After a series of successful pilot scale tests the process has been realized in a first full scale plant in Bad Rappenau (FRG) for the treatment of 170 m^3/h.

KEYWORDS

CARIX process; combined nitrate/sulfate/hardness elimination; partial demineralization; drinking water; carbon dioxide.

INTRODUCTION

Nitrate in drinking water has become a problem since the groundwater of an increasing number of waters supplies has elevated concentrations. These are caused by the too extensive application of fertilizers in agriculture. The problem stems from the fact, that in the human body nitrate ions can be converted to nitrite, which is injurious for health (Rohmann and Sontheimer, 1985). In order to protect the consumers, a standard of 50 mg/l has been introduced in the countries of the European Community (Richtlinie des Rates der EG, 1980). As a consequence of this limitation many water supplies have to reduce the nitrate content of their water. In the absence of low nitrate ressources, this can only be done by either physico-chemical or biological treatment steps.

Application of ion exchange processes is one of the technological possibilities. Nitrate can be removed by three different conventional methods (Clifford and Weber, 1977, Roennefahrt, 1983, Schmitt, 1984):
i) anion exchange against chloride ions;
ii) anion exchange against bicarbonate ions;
iii) demineralization of a bypass and blending with untreated raw water.

Apart from individual differences, these conventional processes have the common disadvantage, that the quantity of salt in the effluent of the regeneration step is by far larger than the quantity which was eliminated during the service cycle. If the water volumes to be treated are big, environmental problems may arise from discharging these effluents into bodies of water.

THE CARIX PROCESS

This disadvantage is avoided in the CARIX process. CARIX (=CArbon dioxide Regenerated Ion eXchange resins) uses a combination of a weakly acid resin in the free acid form and an anion exchanger in the bicarbonate form. Usually the two resins are stored in a mixed bed. In the service cycle neutral salts are replaced by carbonic acid from which CO_2 can be degassed (Höll and Kiehling, 1982 and 1984, Höll, 1985):

$$\frac{\overline{R_c= (COOH)_2}}{\overline{R_a= (HCO_3^-)_2}} + Ca(NO_3)_2 \underset{\text{(regen.)}}{\overset{\text{(service)}}{\rightleftharpoons}} \frac{\overline{R_c= (COO^-)_2Ca^{2+}}}{\overline{R_a= (NO_3^-)_2}} + 2\ H_2CO_3$$

For regeneration the above exchange is directly reversed. Carbonic acid is generated by dissloving CO_2 under pressure in water and is conducted across the mixed be filter. By this means both resins are reconverted to their original forms. Unlike in conventional processes both ions of the regeneration chemical are consumed for regeneration. Thus the amount of salt in the effluent is the same which was removed in the service cycle. Carbon dioxide is required in excess, however, this excess can either be recovered or it can escape into the atmosphere. Therefore there is no increase of salt in the effluent due to unspent regeneration chemicals.

Since carbonic acid is only a weak acid yielding in relatively small concentrations of protons and HCO_3^- ions, its regeneration efficiency is limited. There is no complete conversion of the resins to the free acid and the bicarbonate forms. Part of the functional groups of the exchangers remain loaded with calcium/magnesium and with sulfate/nitrate ions. As a consequence the process allows only a partial demineralization of water.

However, with respect to the treatment of drinking water, this is not a drawback, since drinking water must not be completely demineralized.

Elimination of neutral salts as indicated in the fundamental formal equation of the process principle occurs only, if there are equivalent exchange rates in the filter. If there is an excess of cation exchange an additional softening/dealkalization takes place. In case of an excess of anion exchange, an additional exchange of sulfate, nitrate, and chloride against bicarbonate occurs. Such a non equivalent elimination of cations and anionsis mainly due to the according quantities of the exchange resins in the filter. This fact enables CARIX to be adapted to individual treatment objectives or raw water qualities. If the objective is the predominatn softening with dealkalization, accompanied by a comparatively small reduction of the concentrations of nitrate and sulfate, then the volume of the cation exchanger in the mixture has to be large. If the elimination of anions of strong acids is to be emphasized, the anion exchanger volume has to be selected in a way, that there is approximately an elimination of neutral salts. A further increase of the anion exchanger volume should be avoided, since the pure sulfate/nitrate exchange against bicarbonate ions might lead to the precipitation of solid $CaCO_3$ within the resin filter (Höll, Kretzschmar, and Steeb, 1986).

TECHNICAL SCALE TESTS

The CARIX demineralization principle was first tested in laboratory scale plants in different water works at throughputs up to 150 l/h. Tests with particular respect to nitrate removal were carried out in Bocholt (FRG), where the raw water contained about 1.4 mmol/l NO_3. Details about the test series are given in previous publications (e.g. Höll and Feuerstein, 1985a). The results of these tests demonstrated that CARIX allows a sufficient removal of nitrate, but also of sulfate and calcium/magnesium. Thus it might be applied in the treatment of drinking water.

The further development of the process until technical applicability took place within a cooperation and licence contract with the WABAG company from Kulmbach (FRG). A mobile pilot plant was constructed for throughputs of up to 5 m^3/h and CO_2 pressures of up to 10 bar. This plant which contained about 700 liters of resin mixture was operated in different water works in the Federal Republic of Germany with different objectives of treatment (Feuerstein and co-workers, 1985, Feuerstein and Höll, 1985).

Tests with respect to nitrate removal were carried out in a water work with a raw water containing 1.5 mmol/l of nitrate and 1.3 mmol/l of sulfate. Nitrate content was to be reduced below the EC standard. For these experiments a resin mixture consisting of 166 liters of cation exchanger and 500 liters of anion exchanger (corresponding to a ratio of volumes of V_c/V_a = 1:3) was used. CO_2 pressure during regeneration was 5 bar. Breakthrough curves of one of these experiments are plotted in Fig. 1. Initially the nitrate concentration is reduced to about 30 mg/l, after a throughput of 35 bed volumes the limit of 50 mg/l was exceeded. Within the same period the sulfate concentration was reduced by approx. 75%. In these tests about 20% of the raw water were used for regeneration and rinsing. The consumption of carbon dioxide was in the range of 0.7 to 1.o kg/m^3 of product water.

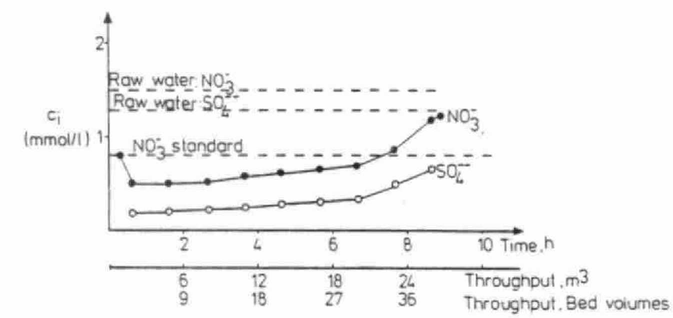

Fig. 1: Breakthrough curves from pilot scale experiments

Although the maximum throughput was only in the range of 30 to 40 bed volumes of raw water until the limit of 50 mg/l was exceeded, the results indicated that CARIX allows a partial demineralization of water including nitrate removal which is both sufficient and economic for the treatment of drinking water.

FULL SCALE REALIZATION

Pilot scale experiments had also been carried out with the Water Supply Group "Mühlbach" around the city of Bad Rappenau. In this region the groundwater contains about 5.4 mmol/l of calcium and magnesium (equalling a hardness of 540 mg/l) and about 40 mg/l of nitrate, which has strongly increased during the last five years. Based on the promising results of these test series, the Water Supply Group decided to build a CARIX plant for the treatment of 170 m^3/h. The objectives of treatment were:
i) the reduction of hardness to 2.7 mmol/l (=270 mg/l), and
ii) the reduction of the nitrate concentration to 25 mg/l.

A flow scheme of the plant is given in Fig. 2. A total resin quantity of 99 m^3 is stored in three filters, each containing 18 m^3 of cation exchanger and 15 m^3 of anion exchanger. Two of the filters are always operating in the service cycle, whereas the third one is regenerated. Thy cyclic switch of the filters is as follows: Each filter remains in the service cycle until a maximum throughput of 44 bed volumes of raw water. After half of this throughput the second filter goes into service and the third one is regenerated, and so on. As a consequence, one filter is always operating along the first half of the breakthrough curves the second one along the second half. The mixed product water of the two filters goes into a degasifier, in

which unspent CO_2 is degassed and the carbonate balance is adjusted..Regeneration is carried out in counter flow using carbonic acid from a separate vessel, which is kept under a CO_2 pressure of 5 bar. The spent regenerant passes a vacuum degasifier in which the major part of the unspent CO_2 is recovered and pumped back into the regenerant tank.

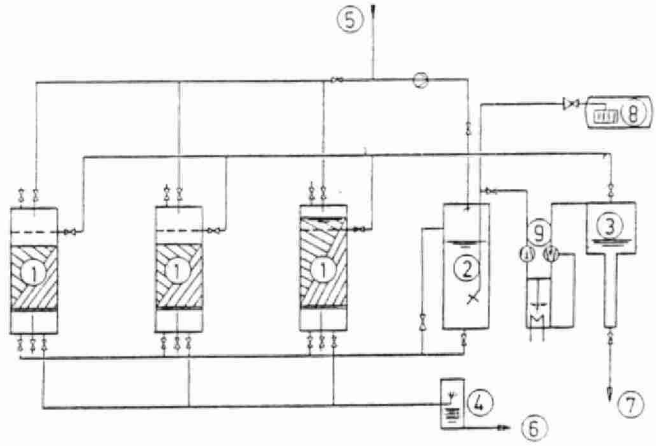

Fig. 2: Scheme of the CARIX plant in Bad Rappenau. 1 = resin filters, 2 = carbonic acid vessel, 3 = vacuum degasifier, 4 = product water degasifier, 5 = raw water, 6 = product water, 7 = waste water, 8 = CO_2 stock, 9 = CO_2 recovery device.

Construction of the plant was started in fall 1984 and in february 1986 the plant went into the production of drinking water. Figure 3 shows a view of part of the installation.

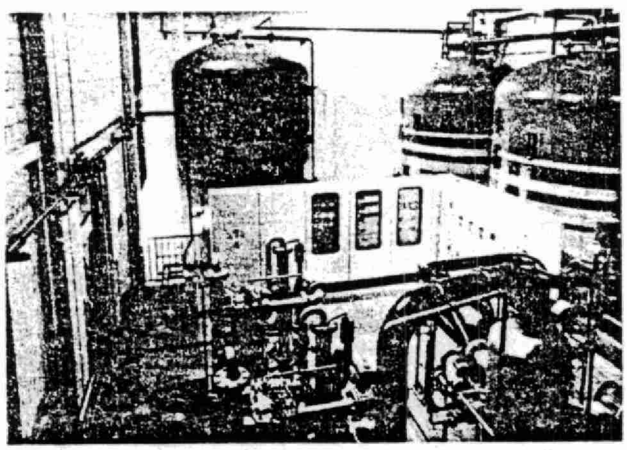

Fig. 3: View of the CARIX plant in Bad Rappenau with the regenerant vessel (top left), two of the filters (top right), the control board (centre), and the CO_2 recovery devices (bottom).

In accordance with the original objectives the concentration of nitrate is reduced to about 25 mg/l whereas the softening is even better than intended since the concentration of calcium and magnesium is diminished to only 2.4 mmol/l (=240 mg/l hardness) as becomes obvious from figs. 4 and 5. Regeneration and rinsing require about 10% of the raw water. Part of the regenerant solution and the rinsing water are reused for regeneration. The waste water which contains the salt is directely conducted to the river Neckar.

The consumption of CO_2 amounts to 0.35 kg/m^3 of product water, that of electric energy to 0.2 kWh/m^3. Based onprices of DM 300.- per ton of CO_2 and of DM 0.2/kWh for electric energy, the specific operation costs (including manpower) are DM 0.15 per m^3 of product water. The total costs for the plant, the building and a 1200 m^3 reservoirwere DM 7,300,000.-. The construction of this first CARIX plant was supported by both the German Ministry of Research and Development and the State of Baden-Württemberg by a total of DM 5,600,000.-. Thus the capital costs are only DM 0.12/m^3. The cost of the treatment by the CARIX plant are outweighed by two facts:

i) the consumption of detergents can be reduced by 40%, and

ii) home softeners, causing additional costs in the range of DM 2.50/m^3 are no longer necessary.

TESTS WITH NITRATE SELECTIVE RESINS

With respect to the removal of nitrate ions, conventional anion exchange resins have the common disadvantage that bivalent anions like sulfate are generally preferred over monovalent ions like nitrate. Thus the operating capacity for nitrate becomes small if the raw water contains too much sulfate (BAYER AG, 1965).

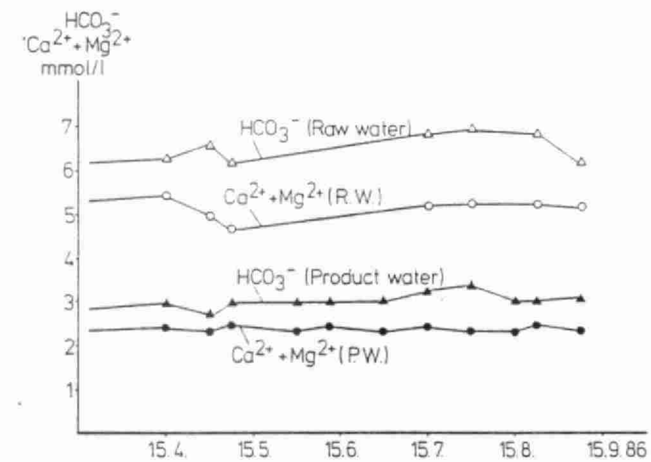

Fig. 4: Development of alkalinity and total hardness in the raw and product water during the first half year of service.

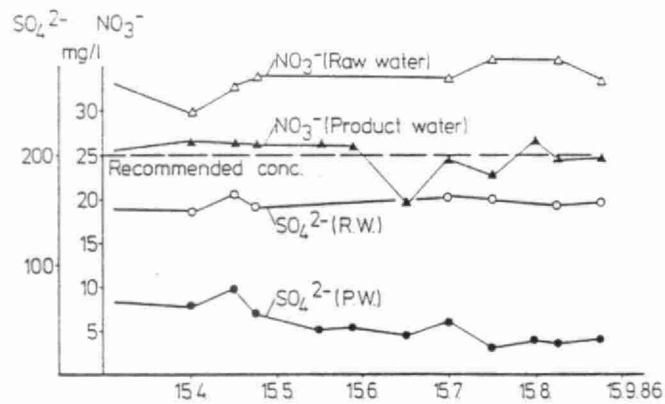

Fig. 5: Development of nitrate and sulfate concentrations in the raw and product water during the first half year of service.

During the last years various attempts have been made to overcome this drawback. The selectivity for nitrate can be improved by reducing the total capacity of the resin. As a consequence the distance between two functional groups becomes larger which hinders the sorption of bivalent anions. A resin of this type is AMBERLITE IRA 904 (Cox and co-workers, 1981). However, since this resin is very strongly basic, the efficiency of regeneration with CO_2 was very poor, yielding in no promising application. Another possibility of generating nitrate selective resins is the introduction of stronger hydrophobic groups into resins of usual capacity (Guter, 1982). An exchanger of this type is AMBERLITE IRA 996. Figure 6 shows the binary sulfate/nitrate equilibrium, which visualizes the preferred uptake of nitrate ions.

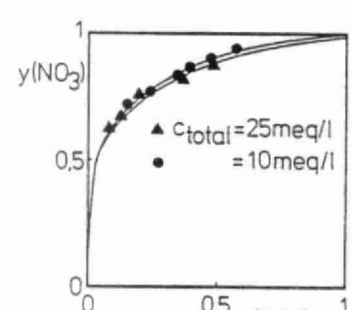

Fig. 6: Binary equilibrium of the NO_3^-/SO_4^{2-} exchange on AMBERLITE IRA 996.

Tests with this resin in the laboratory and the pilot scale demonstrated the general disadvantage of each resin with particular affinities towards certain ions: The preferred uptake of these ions leads to losses in regeneration efficiency. If a resin mixture with this anion exchanger is regenerated in the described way only by CO_2 and water, the effective capacity, which can be produced does not lead to an economic NO_3^- removal. $CaCO_3$ has to be added in the regeneration step (Höll and Kiehling, 1984) in order to generate

sufficient HCO_3^- concentrations in the regenerant solution. By this means, an improved nitrate elimination is achieved, however, a filter for removing suspended solids from the waste water might become necessary (Höll, 1987).

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The CARIX® Process for Removing Nitrate, Sulphate and Hardness from Water
Le procédé CARIX® d'élimination des nitrates, du sulfate et de la dureté de l'eau

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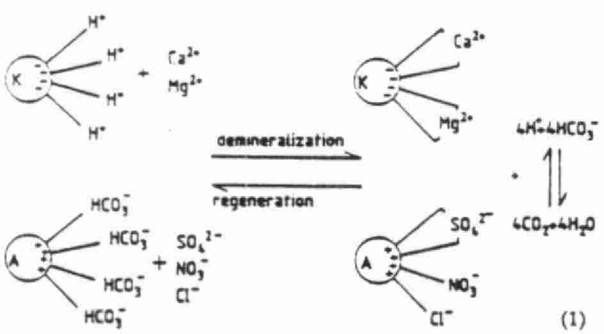
Introduction

A method suitable for the preparation of drinking water was developed during 1978 and 1982 at the Karlsruhe (KfK) Nuclear Research Centre. This method effects the partial softening of water and the removal of nitrate and sulphate with the help of ion exchangers.[1-4] The further development of the method for technical application was carried out by WABAG in Kulmbach. The method is called the CARIX process.

The principle of the CARIX process is based on the use of ion exchange processes. The required processes are carried out with a weakly acidic exchanger in the acid form and an anion exchanger in the HCO_3^- form. Both exchangers are employed together in a mixed bed and are regenerated together in one operation with carbon dioxide. The process has been tested in a pilot plant in several waterworks using a mobile experimental plant, and it was found that it can be used for an economical partial demineralisation of drinking water. The first centralised large scale plant for softening water and reducing the nitrate content was constructed in Bad Rappenau (FRG) and started operation in January 1986. The plant was conceived to treat 170 m^3/h.

The principle of the CARIX process

The CARIX process is based on the combined use of a weakly acidic exchanger in the free acid from and an anion exchanger in the HCO_3^- form in a mixed bed.[2-4]



(1)

In contact with raw water containing dissolved salts, the exchangers remove neutral salts from solution and liberate equivalent amounts of carbon dioxide. When the exchange resins are exhausted, they can be regenerated by bringing them into contact with a concentrated carbon dioxide solution. In contrast with conventional mixed bed processes, the resins in the CARIX process need not be separately regenerated because each of the mixed resins favourably influences the regeneration of the other. As can be seen from equation (1), only the salt removed from the water during the service phase is released into the regeneration effluent. In contrast with conventional exchange processes, the regeneration chemicals do not increase the salt load of the regeneration waste water. When the concentration of dissolved $CaCO_3$ and $CaSO_4$ exceeds saturation, the amount of dissolved salts in the waste water is less than the amount removed from the raw water. For this reason, the process is particularly environmentally compatible.[4,5]

A substantial property of the CARIX process is the influence of the volumetric ratio of the two exchangers on the type of demineralisation.[6] Thus it is possible to vary the ion exchange properties of the mixed bed. When the filter contains a high proportion of the anion exchanger, the anions of stronger acids are eliminated together with neutral salts in exchange for HCO_3^- ions.

When the proportion of cationic exchanger is increased, an additional decarbonization occurs. If the main aim lies in decreasing the anion concentration in the water, a mixture with a high proportion of anion exchanger must be used and the regeneration can be carried out in the presence of $CaCO_3$ in order to increase the pH value. When alkaline earths mainly have to be eliminated, the proportion of cation exchanger must be higher and the regeneration should be carried out without the presence of $CaCO_3$.

Due to the fact that the type of demineralisation can be influenced in this way, the process can be modified to suit raw waters containing different types and concentrations of salts, or modified to achieve a particular water treatment aim merely by selecting suitable exchangers or by changing the ratio of the two ion exchanger in the mixed bed. The combined neutral salt elimination/decarbonisation has a favourable effect on the product water because the ratio of the concentration of hydrocarbonate to that of anions of stronger acids does not change very much. After the CO_2 produced during the demineralisation step has been removed, the water produced possesses, from a corrosion chemical point of view, favourable properties. As a result of being able to vary the extent of neutral salt elimination and decarbonisation it is also possible to change the ratio of carbonate hardness to non-carbonate hardness with the CARIX process, which is principally not possible with other processes with which a complete demineralisation of a part of the water is effected.

Description of the operation of a CARIX plant

The process is shown schematically in Fig. 1. The raw water (5) enters the top of the filter and flows through the bed in a downwards direction.

In the scheme, the filter (1) on the left is in operation and the filter (1) on the right is being regenerated. Regeneration and operation alternate in such a way that one filter is always in operation while the other filter is being regenerated.

After passing measuring and control devices, the water is distributed on to the filter in service and permeates through the mixed bed consisting of a weakly acidic cation resin and a strongly basic anion resin. The water leaves the filter, flows through further measuring and recording devices and degasifi-

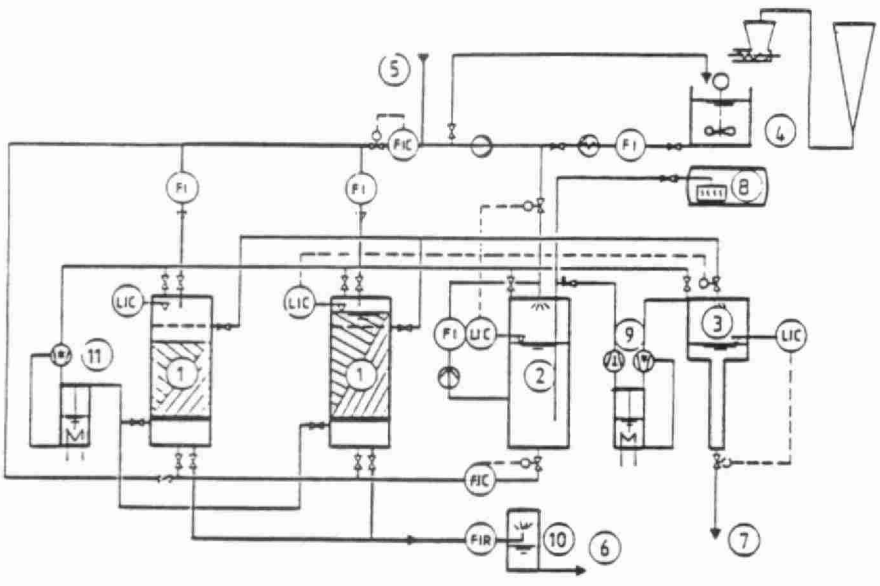


Fig. 1. Scheme of an alternating-step plant, single-stage

cation is effected in the CO_2 degasifier (10) where all the excess carbon dioxide is removed. The purified water (6) is ready for distribution.

The filter is regenerated with a fluidised bed process. The regeneration solution is prepared in the reaction tank (2) and its composition is dependent on the raw water analysis and the required quality of the product water. In the case of nitrate elimination, the solution is prepared from raw water (5), CO_2 from the storage tank (8), retrieved excess CO_2 from (9) and a suspension of calcium carbonate produced in the $CaCO_3$ feeder (4). $CaCO_3$ addition is not needed when the main function of the plant is water softening.

The internal circulation of the regeneration solution is carried out with a circulation pump. The regeneration solution is pumped from the reaction tank (2) into the exhausted filter [the right hand filter (1) in the flow diagram] where the counter current of regeneration solution regenerates the resin bed. The solution leaves the filter at the upper part at the side of the filter as eluate (dashed line). During the regeneration operation, the level of the regeneration solution is held constant by means of a level control. The eluate (= regeneration waste water) passes to the vacuum degasifier (3) where the CO_2 is released from the eluate. The eluate degasifier and the pure water degasification chamber can be united to a compact unit. The CO_2 retrieved from the eluate is passed back to the reaction tank (2) via the CO_2 vacuum/compression unit (9). With the help of a CO_2 circulation pump a portion of the gaseous CO_2 is permanently recirculated to effect an agitation of the resin. In this way, an agglomeration of the resin layer during regeneration is prevented.

The complete regeneration procedure as described above takes about 3½ – 4 h to perform. After the operating filter has been in operation for about 5 h the other freshly regenerated filter is brought into operation as well, so that the first one can be taken out of operation when its capacity has been exhausted. Thus with two filters, a continuous production of purified water is guaranteed; while one filter is in operation the other filter is being regenerated or is standing by for use. In this way, the plant can always run at nominal capacity.

Partial results of the pilot experiments[5]

Nitrate reduction as the main aim — an example

Investigations were carried out in one water works with the aim of reducing the level of nitrate in drinking water. During the experimental period, raw water was available which had a nitrate content of 1.33 ± 0.22 mol/m^3 $\triangleq$ 82.5 ± 13.6 mg/l and a sulphate content of 1.25 ± 0.34 mol/m^3 $\triangleq$ 120.0 ± 32.6 mg/l. The resin mixture consisted of 166 l Amberlite IRC 50 and 500 l Lewatit M 600 corresponding to a volume ratio $C:A = 1:3$.

The filling level in the filter was 1.33 m and the throughput $Q = 3$ m^3/h which corresponds to a filtration velocity of $V_F = 6$ m/h.

In order to be able to judge the results of the treatment, the amount of denitrified water which could be produced, before the nitrate-limit of 0.8 mol/m^3 NO_3 was reached, was used as a measure of the performance.

A typical result of the partial demineralisation experiments is shown in Fig. 2. Due to the fact that the produced water in this case was collected in a storage tank before delivery, the salt concentrations in the mixed water calculated from individual analyses of the effluent are plotted against time and the throughput. Corresponding to the higher affinity of the anion exchanger for bivalent ions, sulphate was removed better than nitrate. The nitrate concentration in the mixed product water reached the EEC limit after about 40 bed volumes. The sulphate content was simultaneously reduced by 72%.

The investigations on the optimisation of the regeneration conditions showed that an addition of a $CaCO_3$ suspension was favourable to the regeneration of the anion exchanger because it caused an increase in the HCO_3^- concentration in the regeneration solution. As a result, the run-time could be improved and the residual nitrate concentration decreased by 30%. The regeneration was carried out with 6 bed volumes of raw water.

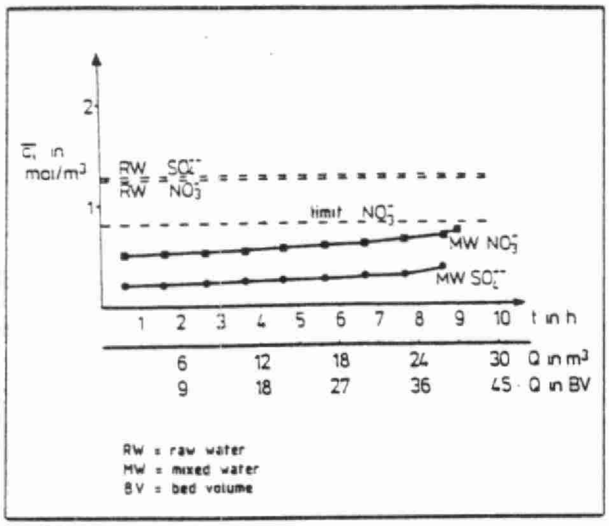


Fig. 2. Course of mixed water concentration in a partial demineralisation test aimed at nitrate elimination (flow rate: $3m^3/h$, volume ratio $C:A = 1:3$)

one bed volume was required for flushing. The regeneration waste water containing about 3 mol nitrate/m³ can be released into the receiving waters without problem.

Large scale realisation

As a result of the findings from the demonstration trials with the pilot plant, the administrative union of the water distribution group in Mühlbach[9,10] decided to install a CARIX plant in Bad Rappenau (FRG) for the purpose of water softening. A simultaneous nitrate elimination was of equal importance in this case.

Erection of the plant was started in November 1984 and the plant was completed in October 1985. It has been conceived for a throughput of 170 m³/h. A total exchanger volume of 81m³ is distributed in three filters, of which two operate at one time to uphold the nominal capacity while the third is regenerated (see the scheme in Fig. 3).

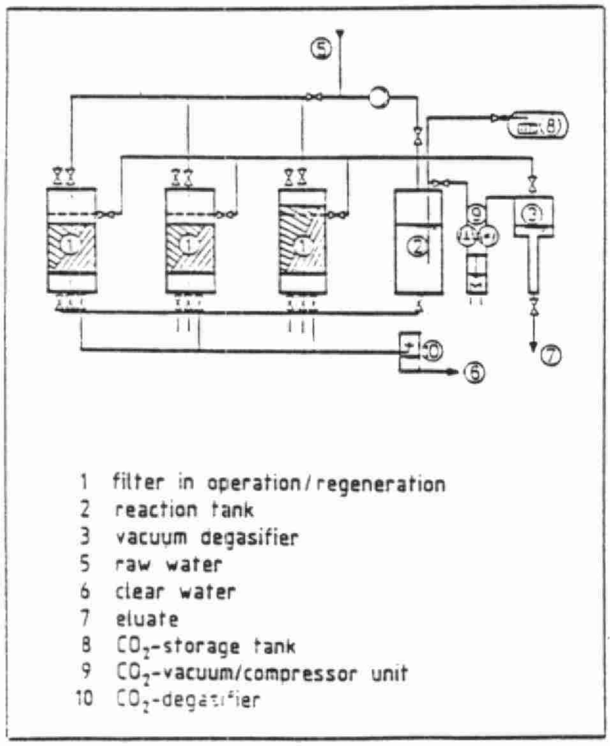


Fig. 3. Simplified scheme of the large-scale plant in Bad Rappenau (FRG)

Each filter is regenerated after treatment of a volume of water equivalent to 31 times the volume of the resin filling. Because the residual salt content in the filtrate increases with increasing run-time the running of the filters is staggered in time and with regard to the remaining capacity of the exchanger. This effects a buffering of the clean water quality (Fig. 4) especially after mixing in the product water reservoir.

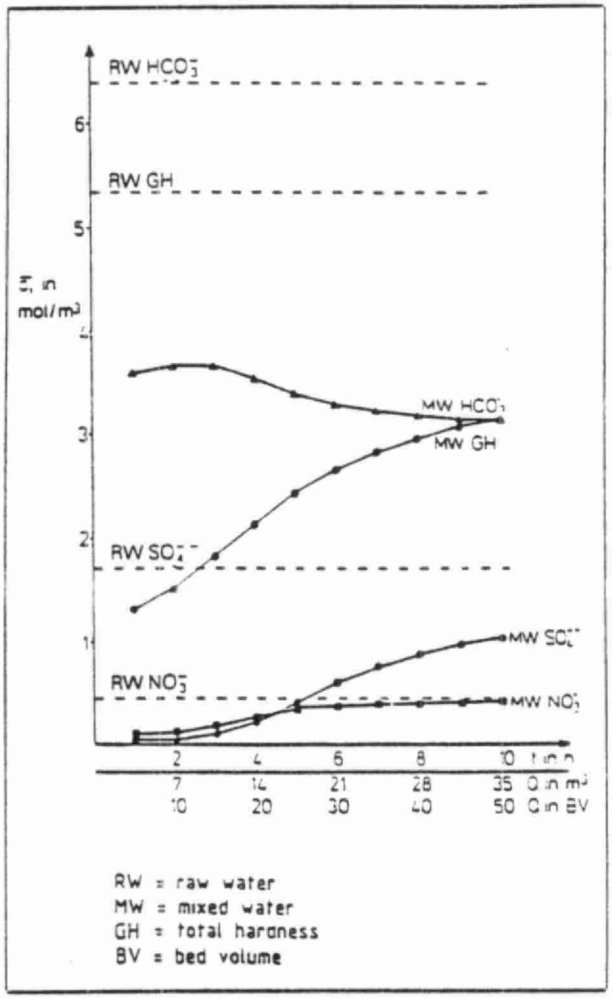


Fig. 4. Course of mixed water concentration in a partial demineralisation test aimed at softening water (flow rate: $3.5 m^3/h$, volume ratio $C:A = 2:1$)

The total cost of the projects amounts to about 7.3 million DM of which 4 million DM are due to the bare exchanger plant. If the exchanger plant is paid off with 12%/year, this alone results in a cost of DM 0.32/m³ of water. With the cost of carbon dioxide being DM 250/ton and including the energy costs for regeneration, compression and degasification a further DM 0.19/m³ have to be added. The cost of treating raw water in the CARIX plant thus amounts to DM 0.51/m³.[8]

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PARTIAL DEMINERALIZATION OF WATER BY ION EXCHANGE USING CARBON DIOXIDE AS REGENERANT PART III FIELD TESTS FOR DRINKING WATER TREATMENT *

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The combined application of a weak-acid ion exchange resin in the free-acid form and of an anion exchange resin in the bicarbonate form allows a partial demineralization of water. The particular advantage of this process is that CO_2 can be used for the simultaneous regeneration of both resins. As a consequence, the effluent contains only the amount of salt which has been eliminated in the service cycle. The present paper discusses results of field tests of the process with a mobile pilot plant in the case of drinking water demineralization.

1. INTRODUCTION

During conventional demineralization of water by strong-electrolyte ion exchange resins the dissolved salts are replaced by water molecules

$$\begin{matrix} \overline{R_c\text{–}H} + Na \\ \overline{R_a\text{–}OH} + Cl \end{matrix} \rightarrow \begin{matrix} \overline{R_c\text{–}Na} \\ \overline{R_a\text{–}Cl} \end{matrix} + H_2O \qquad (1)$$

After exhaustion of the resins, these are reconverted to the free acid and base forms by means of, for example, HCl and NaOH

$$\overline{R_c\text{–}Na} + HCl \rightarrow \overline{R_c\text{–}H} + NaCl \qquad (2a)$$

$$\overline{R_a\text{–}Cl} + NaOH \rightarrow \overline{R_a\text{–}OH} + NaCl \qquad (2b)$$

This kind of regeneration is efficient, yet has two disadvantages: only protons and hydroxyl ions are consumed whereas the coions double the quantity of salt in the effluent. Furthermore, the strong-electrolyte resins require high excess quantities of chemicals for regeneration [1,2].

Various attempts have been made in order to overcome these drawbacks. In the DESAL Process the dissolved salts are replaced by carbonic acid. During regeneration carbon dioxide is used for the conversion of the anion

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exchanger to the bicarbonate form. Since only weak-electrolyte resins are used, only little more than the theoretical minimum of 200% salt is produced [3,4]. Any further reduction of salt quantities in the effluent is possible only if the product compound of the service cycle can be used for regeneration of both resins. This concept has been realized in the Sirotherm process, which in the regeneration step makes use of the increased dissociation of water molecules at higher temperatures [5,6].

Both basic ideas—the exchange of salts against carbonic acid as well as the use of the product compound for regeneration—are combined in the CARIX Process *.

Demineralization

$$\frac{\overline{R_c\text{-}COOH}}{\overline{R_a\text{-}HCO_3}} + NaCl \rightarrow \frac{\overline{R_c\text{-}COONa}}{\overline{R_a\text{-}Cl}} + H_2CO_3 \qquad (3a)$$

Regeneration

$$\frac{\overline{R_c\text{-}COONa}}{\overline{R_a\text{-}Cl}} + H_2CO_3 \rightarrow \frac{\overline{R_c\text{-}COOH}}{\overline{R_a\text{-}HCO_3}} + NaCl \qquad (3b)$$

By the combined application of a weak-acid cation exchanger in the free acid form and an anion exchanger in the bicarbonate form dissolved salts are replaced by carbonic acid. However, if the exhausted resins are treated with carbon dioxide and water, they are regenerated. As is obvious from eqn. (3), the effluent of the regeneration step contains only the quantity of salt that was eliminated during the service cycle. The direction of exchange depends on the CO_2 concentration. At low concentrations elimination of salts takes place, whereas at high concentrations the resins are regenerated.

As was shown in fundamental investigations, the regeneration method leads only to a partial conversion of the resins to the free acid and the bicarbonate forms. As a consequence, the process allows only a partial demineralization of water, as needed, for example, for drinking water treatment. Usually, the effective cation and anion exchange capacities, produced in the regeneration step, are not equal since both exchange processes are not coupled stoichiometrically. Furthermore, filter capacities can be influenced by the ratio of exchanger volumes. Thus, apart from the removal of neutral salts, an additional elimination of either cations or anions occurs. This leads to the possibility of adapting the process to individual problems of water treatment [8–11].

2. TECHNICAL SCALE TESTING

2.1 Process concept

From the formal equation (3), which describes the basic principle of the process, it can be deduced that a close contact between both resins and a common solution will favor elimination of salts as well as regeneration of the resins. In both cases, the simultaneous contact between the solution and the resins keeps the pH at favourable intermediate values [12]. As a consequence, the exchangers should be used in a mixed bed which represents the simplest and most effective technical solution. The two components need not be separated for regeneration, as in conventional mixed beds. Service cycle and regeneration can be realized in a usual counterflow technique. However, during regeneration, precipitation of $CaCO_3$ and $CaSO_4$ may lead to agglomeration of resin material. In order to avoid any kind of scaling, the resin bed has to

* CARIX = CArbon dioxide Regenerated Ion eXchangers [7].

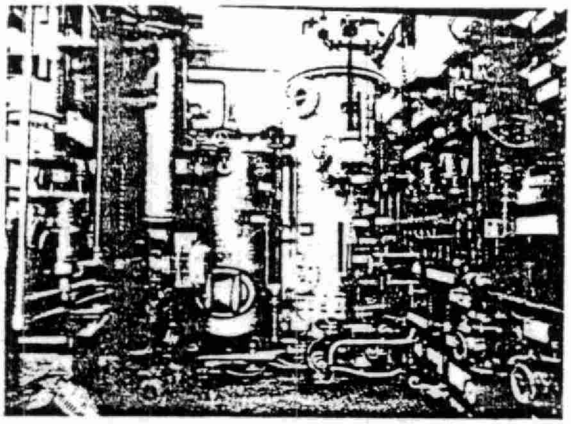

Fig. 1. View of the pilot plant.

be agitated or fluidized during regeneration.

Fundamental investigations about the efficiency of regeneration have shown that a methacrylic resin should be used as cation exchanger. The anion exchange resin must adsorb bicarbonate ions and should be dissociated at pH values of about 7. The best esults have been obtained with strong-base resins of Type II and with acrylic resins.

2.2 *Pilot plant*

After the applicability of the process for drinking water treatment had been proved [10.13], the CARIX Process was to be tested on a technical scale so as to establish if it allows an economic partial demineralization.

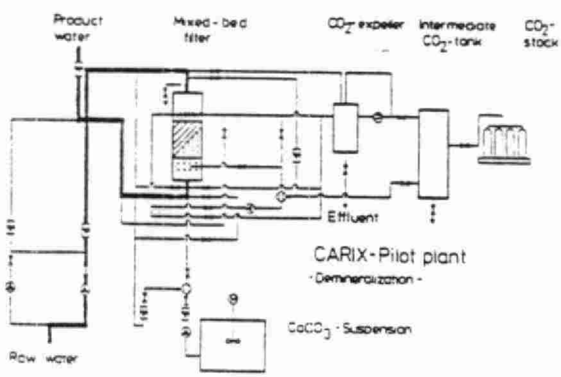

Fig. 2. Flow scheme, service cycle.

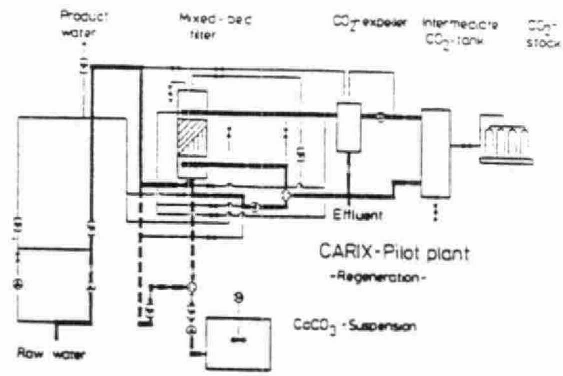

Fig. 3. Flow scheme, regeneration.

In accordance with a cooperation agreement with the Karlsruhe Nuclear Research Center, the WABAG company built a pilot plant for a maximum throughput of 5 m^3/h and CO_2 pressures during regeneration of up to 10 bar. Figure 1 shows a view of the plant. The mixture of 700 l exchanger material is packed in a filter of 0.5 m^2 cross-sectional area and 1.6 m height. During the service cycle raw water percolates from top to bottom (Fig. 2). In the counterflow regeneration step the raw water below the bottom of nozzles is continuously saturated with CO_2 through a superimposed secondary circuit and then pumped through the resin bed together with gaseous CO_2 which fluidizes the resin material (Fig. 3). In order to keep the pH of the regeneration solution at favourable ranges for the conversion of the anion exchanger to the bicarbonate form, a $CaCO_3$ suspension can be fed to the filter. The regenerant leaves the filter through a vent in the top and enters an expeller in which the unspent CO_2 is recovered and pumped back into the intermediate CO_2 tank. This tank is connected with the CO_2 stock.

3. RESULTS OF FIELD TESTS

The pilot plant has so far been tested in several water works in the Federal Republic

of Germany with different objectives. The first experiments were carried out in a water work in which the raw water contains 1.3 mmol/l of nitrate and 1.3 mmol/l of sulfate. The particular objective of these tests was to reduce the nitrate content to below the future standard for drinking water of 0.8 mmol/l (= 50 mg/l). According to the desired elimination of anions, the resin mixture consisted of 166 l of the methacrylic cation exchanger Amberlite IRC 50 and 500 l of the Type II-resin Lewatit M 600, corresponding to a volume ratio $V_c : V_a$ of 1 : 3. Regeneration was carried out with seven bed volumes of raw water at a CO_2 pressure of 6 bar and with addition of $CaCO_3$ suspension. In the service cycle, the rate of filtration was 6 m/h which had been found to be the optimum rate. Figure 4 shows typical breakthrough curves of nitrate and sulfate ions. Nitrate concentration was reduced to about 0.5 mmol/l and the limit of 0.8 mmol/l was reached after a throughput of 35 bed volumes. The sulfate concentration was strongly reduced by 75–80%, owing to the stronger affinity of the exchanger for divalant ions. As is obvious, the quality of the product water is not constant. In order to equalize the concentrations, the product water has to be stored and mixed in a reservoir, the concentrations of which are shown in Fig. 5 as a function of time and throughput, respectively.

The results indicated that a water yield of about 80% is reached. This means that 20% of

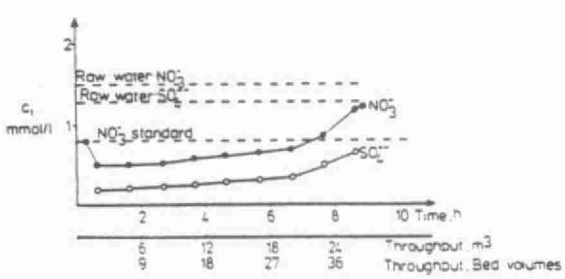

Fig. 4. Breakthrough curves of nitrate and sulfate ions during experiments in the Petershagen Water Works.

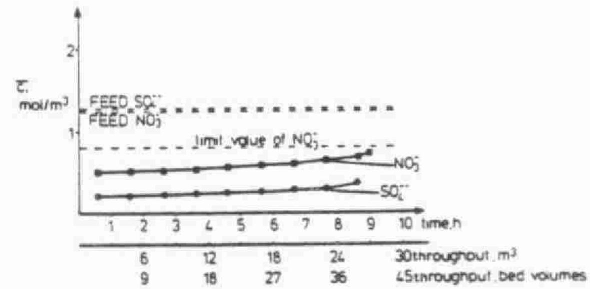

Fig. 5. Development of nitrate and sulfate concentrations in a reservoir, which is supplied by the product water of Fig. 4.

the raw water is used for regeneration and rinsing. Consumption of CO_2 is in the range of 0.7–1 kg/m³ of product water, depending on the pressure and the quantity of $CaCO_3$ added.

In a second application the CARIX Process was tested for the combined elimination of sulfate and alkaline earths. In the te series the raw water contained 2.6–3.1 mmol/ of sulfate and 5.4–6.9 mmol/l of calcium and magnesium. Since the objective was to reduce both cations as well as anions, the resin mixture consisted of 230 l Amberlite IRC 50 and 460 l Lewatit M 600, corresponding to a volume ratio of 1 : 2. Figure 6 shows typical elution curves from one of the regeneration cycles. At the beginning the concentration of sulfate is rather high. However, with advancing conversion to the bicarbonate form it decreases and approaches the raw water concentration. As a consequence of the addition of $CaCO_3$ the concentrations of calcium and magnesium, while measurable, do not indicate the degree of regeneration of the cation exchanger. The development of earth alkaline ions concentrations is a consequence of the regeneration of the anion exchanger: due to the sulfate/bicarbonate exchange the pH slightly drops and, as a consequence, solid $CaCO_3$ is dissolved. With decreasing anion exchange the dissolution of $CaCO_3$ diminishes, too.

Breakthrough curves of the ensuing de-

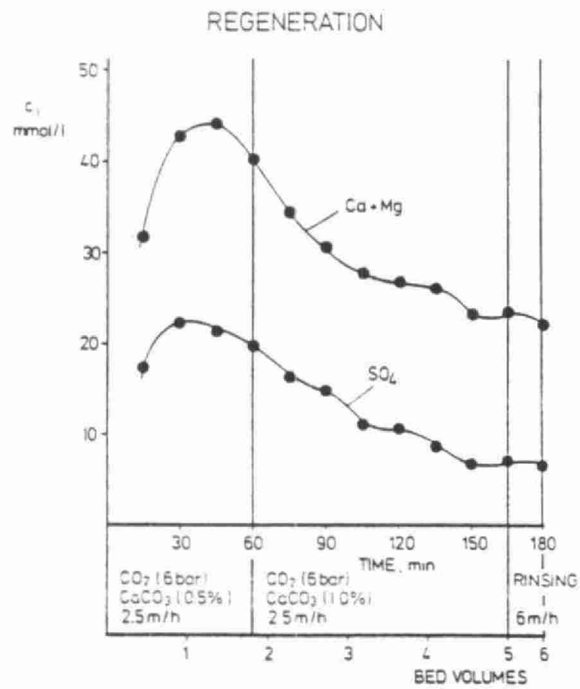

Fig. 6. Development of alkaline earth and sulfate concentrations in the effluent of one regeneration of the experiments in the Münster Water Works.

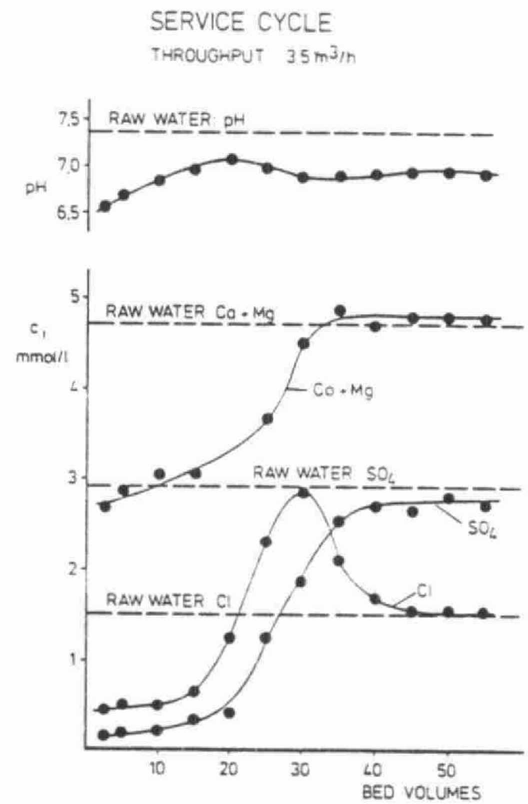

Fig. 7. Breakthrough curves of alkaline earth ions, sulfate, and chloride ions in one of the experiments in Münster.

mineralization are plotted in Fig. 7 as a function of time and throughput. Again, the raw water concentrations of sulfate and hardness are reached after a throughput of about 35 bed volumes. At the beginning of the run chloride ions are also eliminated up to approximately 75%. However, because of the stronger affinity for sulfate ions, chloride is strongly displaced and maximum concentrations of about twice the raw water content occur. The pH is slightly acidic since the product water contains excess CO_2, which is degassed in the CO_2 expeller. In these tests the water yield was about 85% and the consumption of CO_2 was between 0.6 and 1.5 kg/m^3 of product water.

In a third kind of application the process was tested for the predominant reduction of total hardness of a raw water containing 5.0 mmol/l calcium and magnesium. According to the objective, the ratio of exchanger volumes $V_c : V_a$ was again increased and the mixture consisted of 350 l Amberlite IRC 50 and Amberlite IRA 458 each. Since efficiency of the regeneration of the cation exchanger had to be emphasized, no $CaCO_3$ was added, and the pH was thus kept at a minimum value. Figure 8 shows some breakthrough curves plotted as functions of time and throughput.

Initially, the concentration of alkaline earths is strongly diminished by about 75%. However, it increases rapidly parallel to the increase of sulfate concentration in the product water. After sulfate has reached its inlet content there is no further elimination of neutral salts, the process now running as a dealkalization. At the end of the run, hardness is still reduced by about 25%. During the

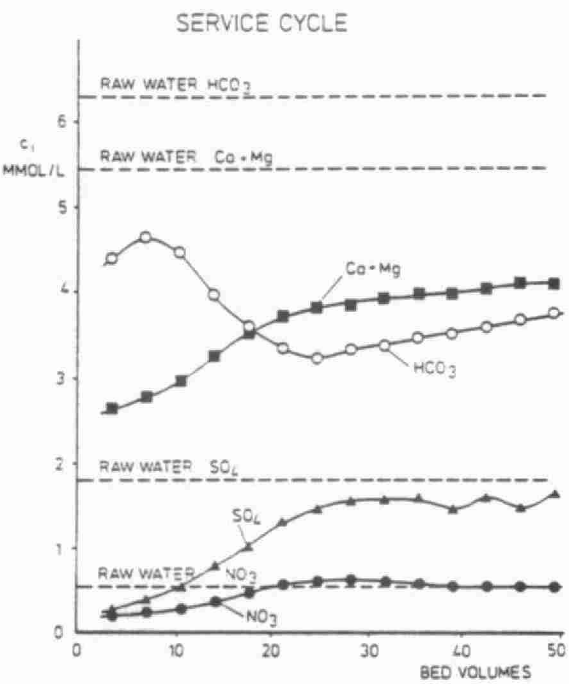

Fig. 8. Breakthrough curves of alkaline earth ions, bicarbonate, sulfate, and nitrate ions in one of the experiments in the Bad Rappenau Water Works.

whole run the concentration of bicarbonate ions is decreased by approximately 50%. The water yield in these test series was again 80–85% and the consumption of CO_2 was about 0.75 kg/m^3 of product water.

The results of these experiments demonstrate that a maximum throughput of about 35–40 bed volumes can be achieved for the elimination of anions and of up to 55 bed volumes for the reduction of alkaline earth cations as follows from some recent tests. Compared to throughputs with conventionally regenerated resins these numbers are rather small. The poor throughputs are a consequence of the limited efficiency of carbonic acid as a regenerant. Nevertheless, calculations of the costs of such a treatment of drinking water have shown that CARIX allows an economic partial demineralization. Based on the results of the above field tests and a CO_2 price of 100 U.S. $/t, the costs for chemicals vary between 6 and 8 ¢/m^3 of product water. Capital costs can be estimated to be in the range of 8 to 14 ¢/m^3, depending on local conditions. Taking into account the small quantity of salts in the effluent, the CARIX process offers of competitive possibility for the treatment of saline raw water which is to be used as drinking water.

The basic advantages of the process concept and the promising results of the field tests have led to the ordering of a first big plant for softening of 170 m^3/h by the Bad Rappenau Water Works, which will go into service in the fall of 1985.

4. CONCLUSIONS

The CARIX Process, which uses a weak-acid cation exchanger in combination with an anion exchanger, represents an excellent method for partial demineralization of wat(The field tests have demonstrated that it ca\ be applied to the treatment of drinking water containing elevated levels of hardness, sulfate, or nitrate, or combinations of these. Other applications in the field of industrial water treatment should be possible.

The process has some particular advantages.

(i) Carbon dioxide, used for the simultaneous regeneration of both resins, is a non-polluting chemical.
(ii) Protons as well as bicarbonate ions of the regenerant are consumed at the same time. Thus, the effluent of the regeneration contains only the same amount of salt that has been removed in the service cycle. Usually this amount is further reduced by precipitation of $CaCO_3$ or $CaSO_4$.
(iii) The filter capacities can be influenced by a suitable choice of the ratio of the exchanger volumes. Thus, the elimination of neutral salts can be superimposed on a removal of either cations or anions (strong electrolytes.

(iv) The product water contains CO_2 in excess. Therefore the post-treatment is very simple.

(v) As a consequence of partial demineralization, the ratio of bicarbonate to mineral acid anions is only slightly altered. Thus, corrosion problems should be avoided.

The results of the field tests have shown that product water salinity is not constant. Therefore the treated water should be stored and mixed in reservoirs in order to equalize quality.

ACKNOWLEDGEMENTS

The authors are indebted to W. Kretzschmar, Dr. K. Hagen, R. Wunderlich and O. Barth of the WABAG company for maintaining the CARIX pilot plant and for the experimental work at the different sites.

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EMERGING WATER SUPPLY TECHNOLOGY AWWARF Code #: WG-02

PROJECT DESCRIPTION

Project Title:

Großversuch zur Grundwassersanierung durch gesteuerte Denitrifikation und aerobe Nachbehandlung im Untergrund
Biological denitrification followed by aerobic underground posttreatment.

Contact (name of person, organization, address, telephone):

Dr. Ing. H.B. Wibbe / Dipl.Ing. Hunke

Stadtwerke Neuss, Hammer Landstr. 45, 4040 Neuss 1

Tel. 02101/206-8134

Germany

Project Description (Please attach a schematic diagram if appropriate):

Durch intensive landwirtschaftliche Düngung im Einzugsgebiet des Wasserwerkes Broichhof weist das in den Gewinnungsbrunnen geförderte Wasser erhöhte Nitratwerte auf. Zur Grundwassersanierung wurde ein Verfahren entwickelt, bei dem gezielt das mit Nitrat am höchsten belastete Grundwasser abgeschöpft und nach Zugabe von Nährstoffen (Essigsäure, Phosphatlösung) in Festbettreaktoren denitrifiziert wird. Anschließend wird das denitrifizierte Wasser belüftet und zur aeroben Nachreinigung wieder in den Grundwasserleiter zurückgeführt.
Nach einer ausreichend langen Bodenpassage wird in den Wasserwerksbrunnen ein nitratarmes Wasser gefördert, das keiner weiteren Aufbereitung bedarf.
Das Verfahren wurde im Pilotmaßstab mehrere Jahre lang erprobt.
Seit Ende 1987 ist eine großtechnische Anlage für eine Denitrifikationsleistung von ca. 7.200 m³/d im Bau. Diese Anlage soll Anfang 1989 in Betrieb gehen.

Removel of NO_3 by biological treatment in a fixed bed reactor with acetic-acid and PO_4^{3-}. After aeration an aerobic underground posttreatment. Extensive pilot plant data available. The big plant goes in operation in '89.

Operating and cost data (including data on efficiency, results, etc.):

1. Nitratgehalt in den Wasserwerksbrunnen	status	60 mg/l NO_3
2. Angestrebter Nitratgehalt	goal	25 mg/l NO_3
3. Wasserwerksleistung		20.000 m^3/d
4. Aufbereitungsleistung		7.200 m^3/d
5. Spez. Raumabbauleistung in den Bio-Reaktoren		3,5 kg N/m^3/d
6. Substratverbrauch (Essigsäure)	Aceticacid	0,32 g DOC/g NO_3
7. Herstellungskosten der Aufbereitungsanlage		8 Mio. DM
8. Spez. Betriebskosten (bezogen auf 5 Mio.m^3/a)		0,15 DM/m^3

Place(s) of installation/application (including dates):

Wasserwerk Broichhof der Stadtwerke Neuss (Adresse siehe oben)
Das Wasserwerk Broichhof deckt ca. 50 % des Trinkwasserbedarfs der Stadt Neuss. Das Waserwerk ist seit 1913 in Betrieb und fördert bisher Grundwasser ohne jede Aufbereitung in das Versorgungsnetz.

Patent staus, if applicable:

Für das Aufbereitungsverfahren besteht kein Patenschutz!

no patent

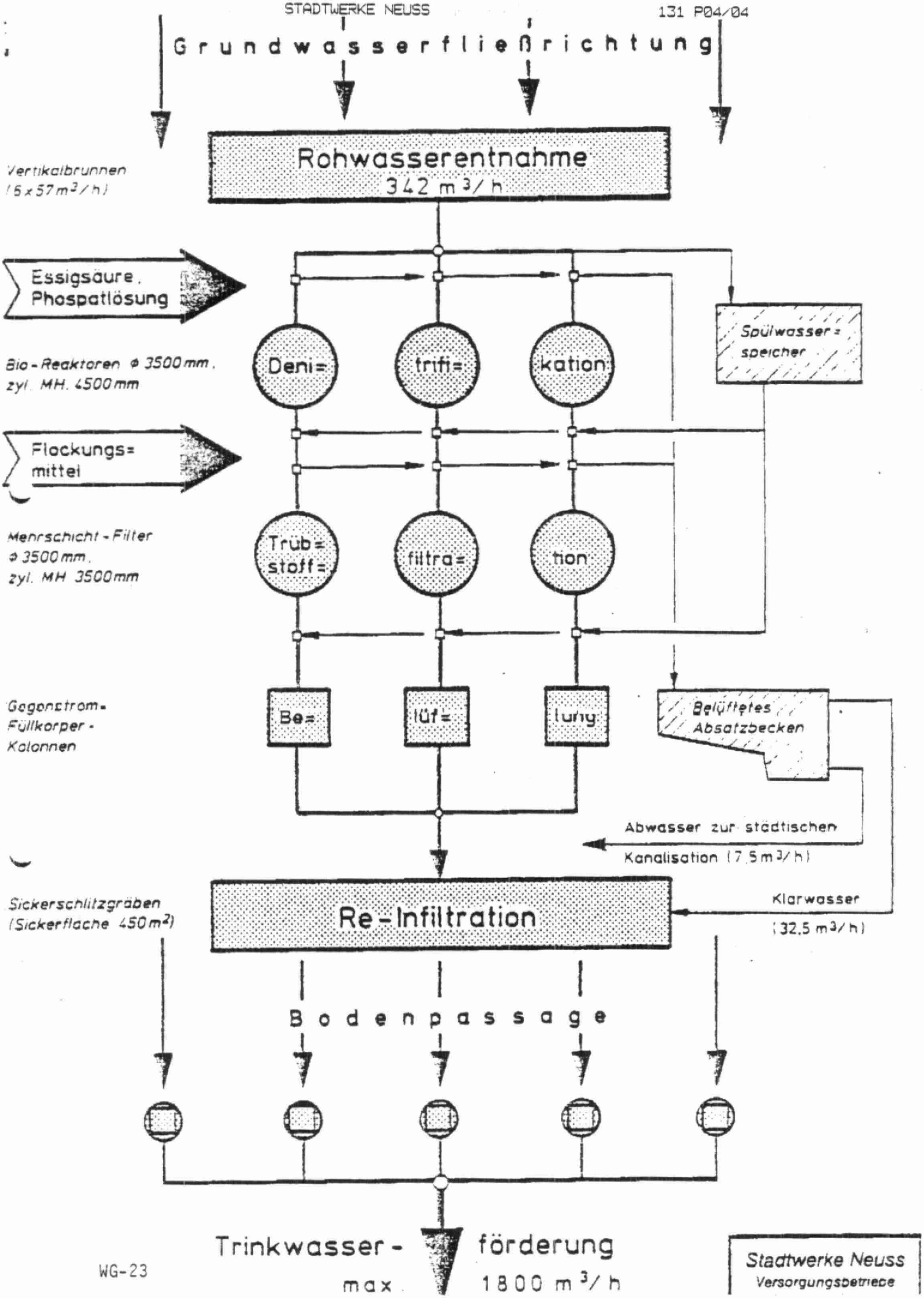
Other information (e.g., funding source, cooperating agencies, etc.):

Das Projekt wird vom Bundesminister für Forschung und Technologie gefördert (FE 02-WT 324/FE 02-WT 8658).

Projektbeteiligte:

Stadtwerke Neuss:	Projektdurchführung
DVGW-Forschungsstelle am Engler- Bunte-Institut der Universität Karlsruhe (TH):	Wissenschaftl. Leitung
Lahmeyer International, Beratende Ingenieure, Büro Düsseldorf:	Ingenieurleistungen

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.


Grundwasserfließrichtung
Rohwasserentnahme
342 m³/h
Vertikalbrunnen
(6 x 57 m³/h)
Essigsäure, Phospatlösung
Bio-Reaktoren ø 3500 mm, zyl. MH. 4500 mm
Deni= trifi= kation
Spülwasser= speicher
Flockungs= mittel
Mehrschicht-Filter ø 3500 mm, zyl. MH 3500 mm
Trüb= stoff= filtra= tion
Gegenstrom-Füllkörper-Kolonnen
Be= lüf= tung
Belüftetes Absatzbecken
Abwasser zur städtischen Kanalisation (7,5 m³/h)
Klarwasser
(32,5 m³/h)
Sickerschlitzgräben (Sickerfläche 450 m²)
Re-Infiltration
Bodenpassage
Trinkwasser- förderung
max. 1800 m³/h
Stadtwerke Neuss
Versorgungsbetriebe

WG-23

PROJECT DESCRIPTION

Project Title:
Automated measurement of the regrowth potential in raw water, treated water and drinking water.

Contact (name of person, organization, address, telephone):

P. Werner; B. Hambsch
DVGW-research center at the Engler-Bunte-Institute, Dept. of Water Chemistry, University of Karlsruhe,
Richard-Willstätter-Allee 5
D-7500 Karlsruhe 1
FRG
telephone: 0721/608-2596

Project Description (Please attach a schematic diagram if appropriate):
The method has been developed to be able to predict the regrowth potential of drinking water. It consists in a microbiological test in laboratory scale by measuring the growth rate of bacteria. The parameter for the increase of biomass during the test is the turbidity at 12° foreward scattering. This measurement had to be automatized to get enough data to calculate the growth rate. The preparation of the water samples for the test is shown in fig. 1. The samples are sterilized by sterile filtration (0,4 µm pore size, Nuclepore filter). A sterile nutrient salt solution is added and the samples are placed into 300 ml-cuvettes of a turbidimeter, measuring at 12° foreward scattering. The samples are inoculated by bacteria washed off from the above mentioned sterile filter. As initial concentration a total cell number of the adapted bacteria between 10^4 to 5×10^4 per ml is adjusted. During the incubation at about 20°C the samples are stirred continuously except for the time when turbidity is measured (normally every thirty minutes). The turbidity measurements were automatized and computercontrolled, the whole set-up is shown in fig. 2.
A typical result of an experiment is shown in fig. 3. This characteristic growth curve is analysed at the end of an experiment by the software of the programme, too. It calculates the growth rate (slope of the growth curve during the logarithmic growth phase) and a growth factor (maximum turbidity to minimum turbidity). This microbiological test is already used in some water treatment plants (see place of installation/application).

Operating and cost data (including data on efficiency, results, etc.):

The growth rate of bacteria in water is a value for the biodegradability of the dissolved organic carbon in the water. If the water is to be distributed a long time, this value has to be very low otherwise regrowth will occur in the distribution system. By measuring this parameter it was possible to optimize a mixing ratio of two different waters so that no regrowth would occur (see publication Werner, Hitsch).
The costs for the equipment are about DM 60.000,-- to DM 80.000,-- with 4 turbidimeters.
Operating costs are quite low, because no expensive chemicals are needed, only the costs for the Nuclepore filters have to be calculated. The man time needed is about half an hour to one hour for every sample (sample preparation, cleaning of the cuvettes and evaluation of the curves).

Place(s) of installation/application (including dates):

One equipment is placed in the DVGW-research center in Karlsruhe, where most of the experimental data have been done. It was installed 1984.

Another equipment works at the BWV (water treatment plant at the Lake Constance), which has a very long distribution system, since 1986.
Another one is in Haifa, Israel, in the frame of a research project, since 1986.
The newest one is in Neuss to control a denitrification plant, since 1987.

Patent staus, if applicable:

None, not planned to apply for a patent.

Other information (e.g., funding source, cooperating agencies, etc.):

The research and development was funded by the BMFT.
Cooperating agency is the Monitek GmbH, the manufacturer of the turbidimeters.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.

Wat. Supply, Vol. 4, Mulhouse, pp. 227–232, 1986.
Pergamon Journals Ltd. Printed in Great Britain.

0735–1917/86 $0.00 + .50

INVESTIGATIONS ON THE GROWTH OF BACTERIA IN DRINKING WATER

P. Werner and B. Hambsch

Engler-Bunte-Institute, Dept. of Water Chemistry, Karlsruhe, F.R.G.

ABSTRACT

In some water treatment plants regrowth in drinking water can only be avoided by disinfection. On the other hand there are a lot of water works which can distribute water without disinfection and which have no problems with high colony counts in the net.

A method is presented to determine the growth rate of bacteria in laboratory scale. The parameters for the increase of biomass during the test are turbidity at 12° foreward scattering and total cell number, determined in the microscope. This microbiological test is able to predict regrowth in drinking water. Moreover the results can be used to optimize drinking water treatment in the water treatment, which helps to minimize the disinfection measures. The principles of the test method are described and the results give evidence of the practical importance of this test.

RESUME

Il y a beaucoup d'eaux potables qui possèdent une tendance à la reviviscence dans le réseau surtout si le temps de distribution de l'eau est prolongué. La raison pour la croissance des bactéries est une concentration des substrats augmentée dans l'eau potable. Normalement la concentration d'un substrat, qui cause une accroissement des microorganismes est très faible et une preuve analytique par des méthodes chimiques est insuffisante. C'est pourquoi un test microbiologique avait été développé, qui est présenté. Les résultats de recherche à l'échelle laboratoire sont comparés à des résultats recueillis de la pratique. La comparaison indique, que ce test simple à éxercer représent une mesure pratique sur la croissance des bactéries dans le réseau de la distribution. On projète de déduire des résultats la dose de chlorure pour la désinfection de l'eau potable. Il est désirable de réduire la concentration de la chlorure à cause de la qualité chimique dans l'eau distribué.

KEYWORDS

Regrowth, turbidity measurement, microbiological test in laboratory scale, growth rate at low substrate concentrations.

INTRODUCTION

Microbial processes are very important in drinking water treatment. The same processes continue in the distribution system, if the drinking water still contains biodegradable organic substances. Therefore a microbiological method for the determination of these substances is necessary. Such a method was developed within the frame of a research program sponsored by the BMFT*. The principle of the method is to measure the growth rate of bacteria in laboratory scale. The parameters for the increase of biomass during the test are turbidity at 12° foreward scattering and total cell number, determined in the microscope (Werner, 1982).

To adapt this method to practical applications the test procedure has to be automatized. This is the only way to collect enough data to be able to control water quality and the efficiency of treatment steps in the water works. Results from an activated carbon plant and the effect of preozonation are presented (Hubele and Topalian 1982; Hubele and Sontheimer 1984). The influence of ozonation on the substrate character of organics dissolved in water can be shown. Moreover, results from measurements in different water works are presented, which confirm the applicability of the method and give evidence to the regrowth in the distribution system.

*) Bundesministerium für Forschung und Technologie

MATERIALS AND METHODS

The preparation of the water samples for the test is summarized in fig. 1 and published elsewhere : detail (Werner, 1985).

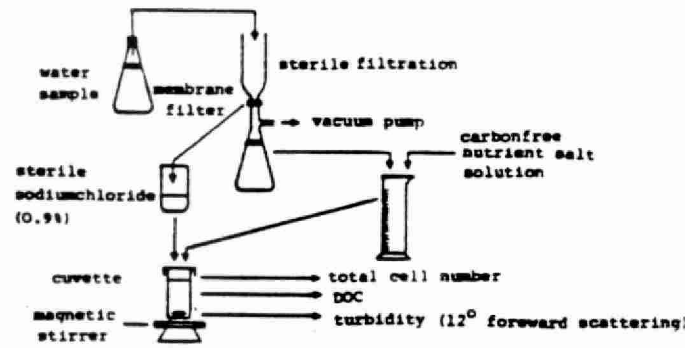


Fig. 1. Preparation of the water samples for the measurement of the growth rate of bacteria.

First, the samples are sterilized by sterile filtration (0,4 µm pore size, Nucleporefilter). A sterile nutrient salt solution is added and the samples are placed into 300 ml cuvettes of a turbidimeter, measuring at 12° foreward scattering. The samples are inoculated by bacteria washed off from the above mentioned sterile filter. As initial concentration, a total cell number of the adapted bacteria between 10^4 to 5×10^4 per ml is adjusted. During the incubation at about 20°C the samples are stirred continously, except for the time when turbidity is measured. To get as many reliable data points as possible and to be able to measure during the 10 to 15 hours lasting logarithmic growth phase without interruption, the turbidity measurements were automatized and computer-controlled. A sketch of the experimental set-up is shown in fig. 2.

Five cuvettes can be analysed in parallel. Every 30 min. twenty values are measured during a time period of 2 minutes and the average is stored by a computer which also controls the entire set up. Thus, an almost continous analysis is possible.

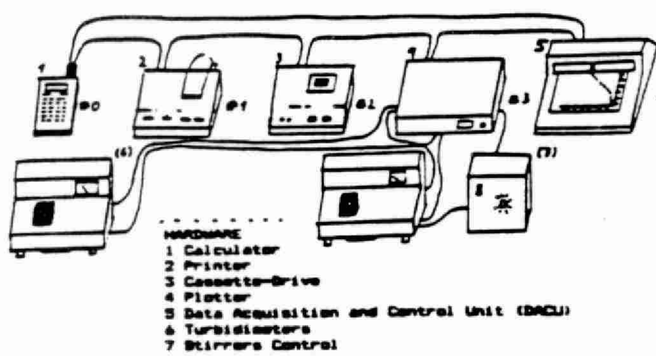


Fig. 2. Automatic equipment for the turbidity measurement.

A typical result of an experiment is shown in fig. 3. A characteristic growth curve can be seen with lag-, log- and plateauphase. It is well known that the morphology and size of bacteria change during the different growth phases. A nutrient broth (initial DOC: 12,7 mg/l) was inoculated with Pseudomonas fluorescens and the growth was measured by turbidity and total cell number. The size of the bacteria decreased during the test (initial: 2,05 µm x 0,95 µm; after 11 hours of incubation 1,3 µm x 0,7 µm). The size was determined by microscopic measurement. The growth rate obtained from the turbidity data is 0,36 h^{-1} (r^2 = 0,99), the one from the total cell number data is 0,35 h^{-1} (r^2 = 0,95). There is a very good correlation between both methods and therefore it is possible to use the turbidity data with all their advantages over cell number measurements (Werner, 1983).

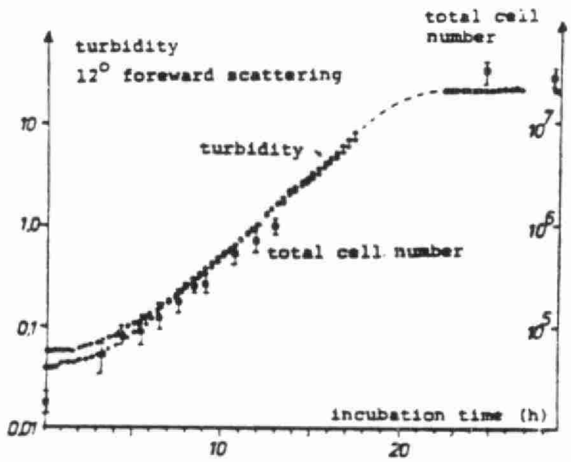


Fig. 3. Multiplication of Pseudomonas fluorescens in nutrient broth, Standard deviations as bars at the values of the total cell number.

EFFECT OF DIFFERENT OZONE CONCENTRATIONS ON THE SUBSTRATE CHARACTER OF NATURAL ORGANIC SUBSTANCES IN WATER

These investigations were performed at an activated carbon pilot plant at the Engler-Bunte-Institute at the University of Karlsruhe with natural humic acids from the Fuhrberg water treatment plant near Hannover (Werner, 1985). Three different ozone doses were investigated in comparison to the untreated humic acids (compare fig. 4, and table 1).

Before preparing the samples as described above the remaining ozone was destroyed by adding sodiumthiosulfate. From every sample different dilutions were tested. The bacteria for the inoculum were taken from an activated carbon pilot plant. The mixed population utilized was already adapted to humic acids. The proliferation of the bacteria was monitored by the increase of turbidity and total cell number. To get a better evaluation of the mineralization of organic substrate by the bacteria the DOC was measured during the test.

As an example for the turbidity data collected with the automatic equipment, the results of the run with 0,5 mg ozone/mg DOC are given in fig. 5.

Fig. 4 shows the increasing growth rates with increasing ozone concentrations. The maximum growth rates μ_{max} and the K_s-values (half velocity concentrations), which are calculated by nonlinear regression to the MONOD-equation are summarized in table 1. The maximum growth rate of the run with 1 mg ozone/mg DOC is 3 times higher than the one of the untreated sample. The K_s-value is the substrate concentration which allows half of the maximum growth rate. In table 1 an "apparent" K_s-value is given, because the parameter used for the characterization of the organic substances is the DOC, which covers all organics present in the water.

However, the bacteria only utilize a more or less small amount of substrate out of the spectrum of organic matter. During the incubation time of 50 hours certainly not all biodegradable organic substances are mineralized, and thus it is not possible, to use this DOC-removal as basis for the calculations of the biodegradable substances. But a good correlation between the biodegraded DOC during the test and the ozone dose can be seen (Werner, 1985). Without ozone treatment only 10 % of the DOC is mineralized, at 1,5 mg ozone/mg DOC the value increases up to 35 %. This ready degradable organic substances are responsible for the growth of bacteria in the distribution system. And this fraction must be removed by treatment steps in the water plant. In the frame of a BMFT-research program these substances are investigated.

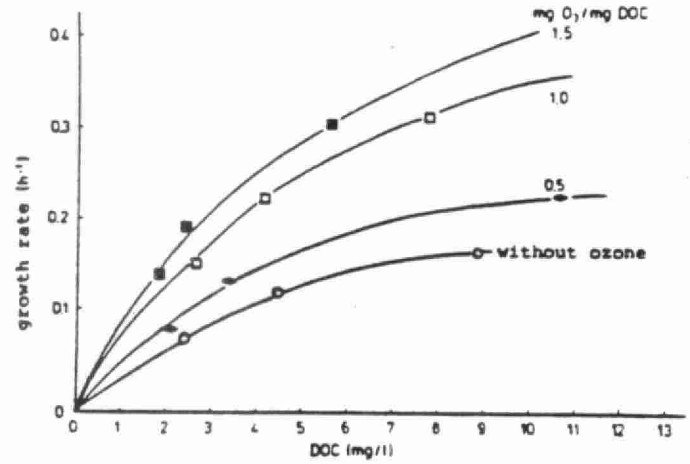


Fig. 4. Effect of ozone on the multiplication of bacteria in a water containing humic acids.

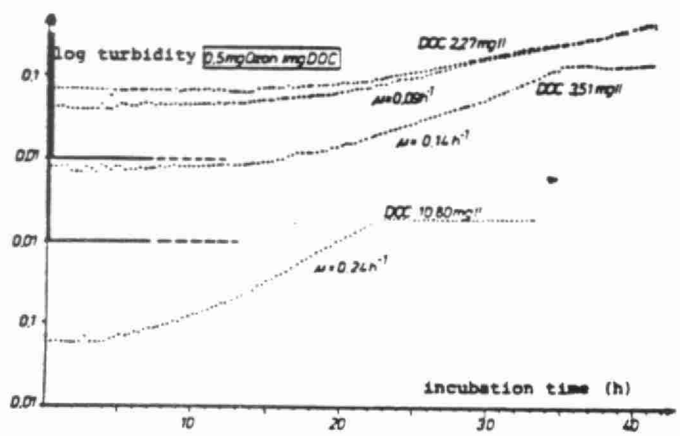


Fig. 5. Increase of turbidity in water containing humic acids after ozonation (0,5 mg O_3/mg DOC)

TABLE 1 Effect of Different Ozone Concentrations on the Mulitplication of

mg Ozone/mg DOC	μ_{max} (h^{-1})	"apparent" K_s (mg/l)	Δ DOC %
C	0,20	4,2	10
0,5	0,38	6,2	25
1,0	0,61	7,7	32
1,5	0,61	5,5	37

PRACTICAL POINT OF VIEW

By investigations in a water treatment plant, where at different seasons regrowth was observed, the applicability of the method could be demonstrated. Two different raw waters were used, on the one hand a ground water which showed a low growth rate of less than $0{,}05\ h^{-1}$ and on the other hand a karst water with a relatively high growth rate of more than $0{,}2\ h^{-1}$.

Utilizing the method a mixing ratio between the two waters could be determined, where no regrowth would occur (Werner, 1985).

This laboratory scale test allows to predict the behaviour of the microorganisms in the distribution system depending on the residence time. In the frame of another BMFT-research program on the applicability of this test a surface water work was investigated for about a year. Almost every month samples were taken from different treatment steps (raw water, water after ozonation, non chlorinated effluent of sand filters). As an example, fig. 6 gives some preliminary results. Although the growth rate varies to a certain extent, a dependence on the season is evident, even up to the effluents of the sand filters. As a rule, the effluent of the filter with the smaller particle size shows lower growth rates than the other one (see fig. 6). This can be explained by the higher microbial activity on the larger surface. Additionally, it is remarkable that the season of low algae counts coincides with the highest growth rates. This phenomena is now investigated.

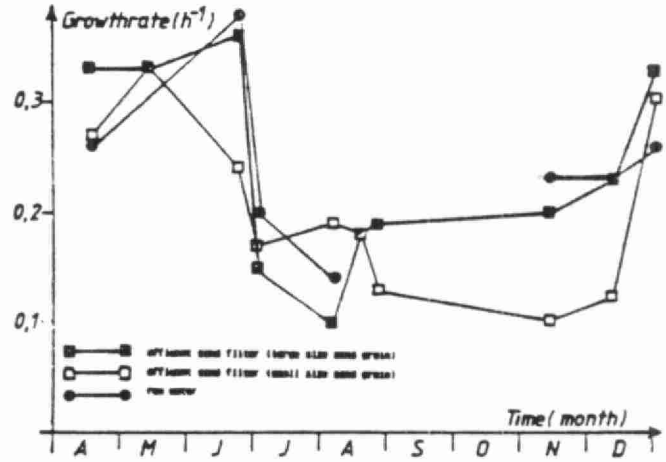


Fig. 6. Seasonal dependence of the growth rate in 1985.

DISCUSSION

Biological processes play an important role in drinking water treatment. For instance, slow sand filters are used for more than a hundred years for this purpose (Noll, 1976). Another example is the biological activated carbon process (Jekel and Sontheimer, 1979; Hubele and Sontheimer 1984). To measure the efficiency of microbial activity of these processes a microbiological test had to be developed because chemical analyses (e.g. DOC) do not yield enough information on biodegradation. Standard microbial methods, as for instance colony counts, can only describe the hygienic conditions, but the purification capacity cannot be calculated from these data.

The characterization of the substrate quality of the organics in a water is of greater interest, because this influences the microbial activity during the above mentioned treatment steps.

Only a microbiological test gives evidence of the regrowth tendency, because as a rule the physiological concentrations of a substrate are lower than their analytical detection limit. The results of such a microbiological test can be used to optimize the drinking water treatment process.

This helps to minimize the disinfection measures, which usually require the addition of chlorine. Chlorine in principle has a negative effect on water quality because AOX (adsorbable organic halogen) and haloforms are produced from the remaining organics in water (Sontheimer 1979).

The reduction of these biodegradable organics remaining in the water can be analysed by the test procedure presented. The goal must be the transfer of the biodegradation into the water treatment plant, which automatically reduces regrowth in the distribution system.

There is an indication that waters with growth rates of less than $0{,}15\ h^{-1}$ measured in the test create no regrowth problems. This means that the generation time is long enough to avoid higher colony counts than allowed by the standards during the usual residence time in the distribution system.

ACKNOWLEDGEMENT

We thank the BMFT for the grant. Thanks are due to Frau Eberhagen and Frau Röthig, which are involved in the experimental part of the research program.

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Probleme bei der Trinkwasseraufbereitung aus Karstwasser

Problems concerning drinking water treatment from carsty water

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Summary

The drinking water supply of Salzburg uses carsty water on the one hand and ground water on the other. In 1983 problems occured with Crenothrix polyspora in the pipe system which were only observed when mainly carsty water was used. In different mixtures of carsty water to ground water the growth rate was measured. At a ratio of 1:4 the value was very low. When distributing water in this ratio no regrowth in the system occured . On the long run a further treatment of the carsty water is necessary. A pilot plant was built with ozonation, flocculation and filtration but the experiences showed that this treatment was not economic.
From the hydrogeological point of view an infiltration and biodegradation in the aquifer was possible and investigations proved this method to be successfull.

Zusammenfassung

Die Stadtwerke Salzburg nutzen sowohl Karstwasser als auch Grundwasser für die Wasserversorgung.
1983 traten Probleme mit Crenothrix polyspora im Leitungsnetz auf, die nur beobachtet wurden, wenn überwiegend Karstwasser verwendet wurde.
Durch Messung der Wachstumsrate von Bakterien bei verschiedenen Mischungsverhältnissen von Karst- und Grundwasser konnte ein Mischungsverhältnis bestimmt werden, bei dem keine Wiederverkeimung im Leitungsnetz mehr auftrat.
Auf lange Sicht mußte jedoch eine weitergehendere Aufbereitung des Karstwassers in Erwägung gezogen werden.
Hierzu wurde eine halbtechnische Versuchsanlage erstellt, die Ozonung, Flockung und Mehrschichtfiltration umfaßte. Diese Aufbereitung erwies sich jedoch als nicht wirtschaftlich, da erst relativ hohe Flockungsmittelkonzentrationen gut absetzbare Flocken ergaben.
Aus den gegebenen hydrogeologischen Verhältnissen bot sich auch eine Bodenpassage des Karstwassers an, um durch biologische Prozesse den abbaubaren Anteil der gelösten organischen Wasserinhaltsstoffe zu reduzieren.
Durch Untersuchungsserien konnte die Effektivität dieser Aufbereitung durch Untergrundpassage nachgewiesen werden.

1. Biologische Probleme bei der Wasserversorgung der Stadt Salzburg

Die Hauptstütze der Wasserversorgung der Stadt Salzburg ist seit 1875 die Fürstenbrunnquelle, die am Untersberg, einem rd. 2000 m hohen Karstgebirgsstock, südlich der Stadt Salzburg, entspringt.

Bei dieser Quelle sind die typischen Karsteigenschaften ins Extrem gesteigert: Schüttungsschwankungen zwischen 50 l/s und 11.000 l/s, damit verbunden Qualitätsänderungen, vor allem zeitweise starke Trübungen durch Höhlenlehm und schließlich ein schwankender, aber immer hoher Gehalt an Huminstoffen. Dieses Quellwasser wird mit Grundwässern vermischt, die in ihrer Beschaffenheit sowohl in sich als auch untereinander sehr gleichmäßig sind und nur sehr niedrige Huminstoff- bzw. DOC-Werte aufweisen.

Solange das Quellwasser in ausreichender Menge und Qualität zur Verfügung steht, wird es im maximal möglichen Umfang zur Versorgung herangezogen. Während der Schneeschmelze kann u.U.

wochenlang ausschließlich Quellwasser verwendet werden. Soweit notwendig, wird dem Quellwasser Grundwasser zugemischt. Seit 1957 wird das zur Verteilung kommende Wasser zur Desinfektion und Schönung mit Ozon behandelt, wobei die über Redoxmessung automatisch gesteuerte Ozondosierung gerade der jeweils maximalen Ozonzehrung nach 4 Minuten Reaktionszeit entspricht. Dazu sind Konzentrationen von 0,4 bis über 3,0 mg/l Ozon erforderlich. Während des Aufenthaltes im Behälter wird das restliche Ozon vor Abgabe des Wassers ins Netz vollständig gezehrt. Dieses Verfahren bewährte sich über ein Viertel Jahrhundert.

Im Sommer 1983 traten in einem Stapeltank eines Getränkeerzeugers in Salzburg viele weiße Flocken bis zu 1/2 cm Länge auf. Bakteriologische Untersuchungen brachten kein Ergebnis, auch Anzuchtversuche mit Pilznährböden und anderen in der Lebensmittel- und Getränkeuntersuchung üblichen Nährmedien waren negativ. Im Mikroskop war ein Geflecht von Fäden erkennbar.

In einem anderen Stadtteil kam es, bedingt durch die Flocken, zu verstopften Filtern in den Hausinstallationen.

Das Leitungssystem wurde sofort in größtmöglichem Ausmaß gespült, aber damit konnte nur eine leichte Verringerung, keineswegs jedoch eine Freispülung erreicht werden. Untersuchungen entlang der Hauptrohrstränge zeigten, daß das Wasser im Behälter noch klar war und die Flockendichte mit zunehmender Verweilzeit im Rohrnetz anstieg. Eine sofort eingeleitete Hochchlorung (1,5mg/l) bis zu 1,5 mg/l Chlor brachte keine Verbesserung. Koloniezahlbestimmungen des sichtlich trüben Wassers ergaben einwandfreie Befunde, womit die Gesundheitsbehörden die Möglichkeit hatten, die weitere Abgabe des Wassers zu dulden.

Nach eingehenden mikrobiologischen Untersuchungen wurden die Flokken als Crenothrix polyspora identifiziert.

2. Vorkommen und Bedeutung von Crenothrix polyspora (COHN)

Crenothrix polyspora wurde erstmals 1870 von COHN im Zusammenhang mit dem Auftreten dieses Bakteriums in der Trinkwasserversorgung von Breslau beschrieben (1). Die Grundform von Crenothrix polyspora ist eine einfache Zellkette, die sich durch Querteilung verlängert und sich in einer Scheide befindet. Diese Fäden wachsen rasenartig nebeneinander und erreichen eine Länge bis zu 1 cm. Bei üppigem Wachstum bilden die Fäden Flocken, die aus einer Vielzahl untereinander verklebter Einzelfäden verschiedenen Alters bestehen. Die Vermehrung erfolgt durch sogenannte Mikro- und Makrokonidien, die in der Regel von einer Schleimkapsel umhüllt sind und massenweise auftreten können.

Die Ursache für das Auftreten von Crenothrix polyspora in Trinkwasserversorgungsanlagen ist bislang noch unklar. Man geht aber davon aus, daß erhöhte organische Belastungen des Wassers die Vermehrung dieses Bakteriums begünstigen. Die Kultivierung von Crenothrix polyspora im Labor ist bislang noch nicht gelungen. Dieses Bakterium hat keinerlei hygienische Bedeutung, stellt aber, bedingt durch die Massenentwicklung, Substrat für die Vermehrung von anderen Bakterien dar, die bei der Koloniezahlbestimmung in Wasserproben erfaßt werden können.

Eine detaillierte Beschreibung von Crenothrix polyspora erfolgte durch BUMB und SCHWEISSFURTH 1981 (2).

3. Lösung des akuten Poblems

Mit der Identifizierung der Trübung als Bakterien-Massenentwicklung lag es nahe, zur Eindämmung die Nährstoffquelle auszuschalten. Zu diesem Zweck wurde das huminstoffreiche Quellwasser durch huminstofffreies Grundwasser ersetzt. Innerhalb weniger Tage war die Trübung wieder beseitigt. In der Folge durchgeführte Untersuchungen zeigten, daß bei Betrieb mit überwiegendem Anteil von Karstwasser Crenothrix polyspora im Rohrnetz und hier insbesondere in den Endsträngen auftrat, während bei Verwendung von Grundwasser allein dieses Problem nicht beobachtet wurde.

Da die Quelle im Normaljahr bis zu zwei Dritteln des Jahresbedarfes der Stadt deckt, kann auf sie nicht verzichtet werden. Es mußten daher Wege gefunden werden, die zumindest eine teilweise Nutzung dieses Karstwasser ermöglichen. Mit der Methode zur Bestimmung der Vermehrungsgeschwindigkeit von Bakterien konnte ein Mischungsverhältnis der beiden Rohwässer ermittelt werden, bei welchem auch nach Ozonbehandlung keine Verkeimung im Netz zu erwarten war (3). Untersucht wurden Grund- und Karstwasser sowie Mischungen dieser beiden Komponenten in Verhältnissen, die in den Abbildungen 3.1 und 3.2 angegeben sind.

Im Karstwasser betrug die Vermehrungsrate 0,2 h^{-1}. Durch den Zusatz von Grundwasser, in dem die Bakterien innerhalb der Bebrütungszeit nicht zu wachsen vermochten, konnte der Wert bei einem Verhältnis von 1:4 unter 0,1 h^{-1} herabgesetzt werden. Die Messungen der Gesamtzellzahlen bei Versuchsbeginn und -ende in den Ansätzen bestätigten dieses Ergebnis.

Der DOC-Gehalt in den Wasserproben nahm während der Bebrütung im Karstwasser um 0,65 mg/l ab. Der abbaubare Anteil betrug 17 %.

Bei dem Mischungsverhältnis 1:4 mit Grundwasser war dagegen keine meßbare Abnahme festzustellen. Bei einer Fahrweise der Wasseraufbereitung mit diesem Mischungsverhältnis kam es in den letzten 3 Jahren zu keiner Verkeimung im Rohrnetz.

4. Langfristige Lösung

Alle Untersuchungen sowie die langjährige Erfahrung der Salzburger Stadtwerke haben gezeigt, daß die Huminstoffe im Karstwasser der Fürstenbrunnquelle eindeutig die Ursache für das Auftreten von Crenothrix polyspora und die gelegentlichen Verkeimungen insbesondere in den Endsträngen darstellen. Als langfristige Lösung ist daher eine Wasseraufbereitung zur Elimination des Huminstoffgehaltes des Karstwassers erforderlich. Hierfür bieten sich einerseits chemisch-physikalische Verfahren (Ozonung, Flockung, Filtration) und andererseits eine Untergrundpassage an.

4.1 Aufbereitung in der Versuchsanlage

Zum Studium einer Flockungsfiltration wurde eine halbtechnische Versuchsanlage für einen Durchsatz von bis zu 1,6 m^3/h mit folgenden Verfahrensschritten aufgebaut:

Ozondosierung - Flockungsmitteldosierung - pH-Wert Korrektur - Flockungshilfsmitteldosierung - Reaktionsbehälter - Filtration über Mehrschichtfilter Sand - Koks - Aktivkohle bzw. Sand - Koks (Abb. 4.1.1.)

Als Flockungsmittel wurden Eisenchlorid, Aluminiumsulfat und Polyaluminiumchlorid in weiten Konzentrationsbereichen jeweils mit

und ohne Ozon eingesetzt. Darüberhinaus wurden verschiedene Qualitäten von Polyacrylnitril-Flockungshilfsmitteln getestet. Erst bei hohen Flockungsmittelkonzentrationen (ab 5 mg/l Eisen) bildeten sich absetzbare Flocken. Auch Ozon und Polyacrylnitril bewirkten keine Verbesserung. Dadurch wird die chemische Aufbereitung des Karstwassers wirtschaftlich sehr unattraktiv.

4.2. Biologische Aufbereitung in Untergrund

Aus den gegebenen geographischen und hydrogeologischen Verhältnissen im Wassereinzugsbereich am Untersberg bietet sich zur Wasseraufbereitung eine Bodenpassage des Karstwassers an, bei der die biologischen Prozesse den abbaubaren Anteil der gelösten organischen Substanzen hinreichend reduzieren. Ein Versuchsfeld mit Versickerungs- und Probeentnahmeeinrichtungen wurde angelegt und die Veränderung der Wasserqualität während der Bodenpassage durch ein intensives chemisches und mikrobiologisches Untersuchungsprogramm überwacht.

Die Transportleitung von der Fürstenbrunnquelle zur Stadt führt durch das Grundwasserfeld Glanegg. Zwischen Quelle und Grundwasserfeld verläuft der Rosittenbach, ein Wildbach, der unmittelbar beim Übertritt aus dem steilen Felsen in den ebenen Talboden in seinem eigenen Schwemmfächer versickert und ganz wesentlich zur Grundwasserneubildung im Grundwasserfeld beiträgt. Die Wasserführung dieses Baches schwankt sehr stark. Nur an wenigen Tagen des Jahres ist die Wasserführung so groß, daß ein Teil des Wassers die Versickerungsstelle oberirdisch im Bachbett verläßt.

Die Zubringerleitung von der Fürstenbrunnquelle kreuzt dieses Bachbett am Beginn der Versickerungsstrecke, so daß es nahe lag,

Karstwasser aus der Leitung hier mit zur Versickerung zu bringen, zumal das Bachwasser und das Quellwasser chemisch und sogar bakteriologisch sehr ähnlich sind.

Für diese Grundwasseranreicherung wurde die wasserrechtliche Bewilligung erteilt und daraufhin zeitweise im Ausmaß bis zu 80 l/s versickert.

Auf Verlangen der Landessanitätsdirektion war besonders Augenmerk darauf zu richten, daß nicht durch die Versickerung des Quellwassers das Crenothrix-Problem in den Grundwasserleiter eingeschleppt wird. Eine Kontamination konnte mittels intensiver Untersuchungen durch das Hygieneinstitit der Universität Wien, in Zusammenarbeit mit der bundesstaatlichen bakteriologisch-serologischen Untersuchungsanstalt Salzburg mit an Sicherheit grenzender Wahrscheinlichkeit ausgeschlossen werden.

Zur Verfolgung der Vorgänge im Untergrund wurden entlang der Fließstrecke drei Kontrollpegel errichtet, die es erlaubten, einwandfreie Wasserproben auch für bakteriologische Untersuchungen zu entnehmen (Abb. 4.2.1). Aus diesen drei Pegeln, sowie dem Quellwasser, dem Bachwasser und dem nächstgelegenen Brunnen wurden wöchentlich Wasserproben entnommen und einer wesentlich erweiterten bakteriologischen und chemischen Untersuchung unterzogen.

Die Ergebnisse einer Untersuchungsserie sind in den Tabellen 4.2.1 und 4.2.2 zusammengefaßt und zeigen, daß die klassischen bakteriologischen Daten eine Abnahme der Werte vom Rosittenbach bis hin zum Grundwasserwerk Glanegg aufweisen. Die Probenahmepegel sind in der Reihenfolge 131, 129 und 130 zwischen Einlaufbauwerk und Grundwasserwerk angeordnet. Lediglich Pegel 129, der

auch die höchsten Trübungswerte aufweist, fällt etwas aus dem Rahmen, da er durch eine andere Grundwasserströmung beeinflußt wird und daher nur bedingt zur Bewertung des Aufbereitungseffektes des Karstwassers während der Bodenpassage herangezogen werden darf.

Bemerkenswert ist, daß alle Werte sehr niedrig sind und selbst im Wasser des Rosittenbaches sehr kleine Koloniezahlen auftreten (Tab. 4.2.1). Dieser Befund ist durch das zum Zeitpunkt der Probenahme trockene und kalte Wetter, bei dem der Bach in der Regel besonders sauberes und klares Wasser führt, zu erklären. Üblicherweise hat das Bachwasser keine Trinkwasserqualität. Erwartungsgemäß ist das Wasser des Grundwasserwerkes Glanegg am geringsten belastet. Erstaunlich ist, daß im Gegensatz zu unseren bisherigen Erfahrungen die Koloniezahlen bei 36 °C Bebrütungstemperatur höher liegen als bei 20 °C. In keiner Probe der fast 2 Jahre lang betriebenen Versickerung konnte Pseudomonas aeruginosa nachgewiesen werden und die Gesamtzellzahlen waren mit Werten zwischen 10^3 und $5x10^4$/ml ebenfalls sehr niedrig. Die Ergebnisse der Fürstenbrunnquelle, die längere Zeit außer Betrieb war und erst kurz vor der Probenahme wieder einspeiste, gelten deshalb nicht als repräsentativ, sind aber sehr klein.

Die Abnahme des DOC-Gehaltes während der Versickerung zeigt ebenso wie die mikrobiologischen Kenndaten deutlich den Aufbereitungseffekt der Untergrundpassage.

Neben den klassischen bakteriologischen Paramtern wurde zusätzlich noch die Vermehrungsgeschwindigkeit von Bakterien im Verlauf der Untergrundpassage gemessen. Die Befunde sind in der Tabelle 4.2.2 zusammengefaßt. Bedingt durch die Wetterlage war die Abbaubarkeit und damit die Vermehrungsrate der Bakterien im

Wasser des Rosittenbaches mit 0,11 h^{-1} recht gering. Je nach Jahreszeit liegen hier die Werte aber wesentlich höher. Bis hin zum Grundwasserwerk Glanegg nehmen die Wachstumsraten ab; im Grundwasserwerk ist keine Bakterienvermehrung mehr festzustellen. Die Gesamtzellzahlbestimmungen in den Ansätzen zur Bestimmung der Wachstumsraten bestätigen den Befund.

Die Ergebnisse der physikalischen und chemischen Parameter sind in den Abb. 4.2.2 bis 4.2.4 dargestellt. Die Wassertemperaturen im Verlauf der Bodenpassage belegen deutlich, daß das versickerte Wasser entlang der Pegel den Boden durchströmt (Abb. 4.2.2). Die Abnahme der organischen Belastung, gemessen über SAK bei 254 nm und $KMnO_4$-Verbrauch, während der Bodenpassage zeigten den biologischen Abbau im Aquifer. Die Werte verringern sich im Schnitt um den Faktor 10 (Abb. 4.2.3 und 4.2.4).

Ein ähnlich guter Aufbereitungseffekt ist sowohl für die DOC- als auch für die Trübungsdaten, die hier nicht im Bild dargestellt sind, zu erkennen.

Zur Überprüfung der seinerzeit rechnerisch ermittelten Fließzeiten vom Rosittenbach bis zum Grundwasserwerk Glanegg wurde durch die Bundesanstalt für den Wasserhaushalt von Karstgebieten in Wien ein umfangreicher Färbeversuch mit Uranin durchgeführt, der eine ausreichende Sicherheitsspane für diese Grundwasseranreicherung erkennen ließ.

Diese Versuche zur Grundwasseranreicherung brachten das Ergebnis, daß durch die Untergrundpassage bzw. Grundwasseranreicherung das Quellwasser ebenso gut aufbereitet wird, wie das schon eh und je dort versickernde Bachwasser, womit eine kostengünstige, sichere und naturnahe Aufbereitungsmöglichkeit für das Wasser der

Fürstenbrunnquelle gefunden wurde.

5. Schlußfolgerungen und Ausblick

Bei der Auswertung der jahrzehntelangen Analysenreihen des Quellwassers konnten noch keine Veränderungen erkannt werden, die die plötzliche Bakterienmassenentwicklung erklären könnten. Trotzdem verhält sich das Quellwasser derzeit im Rohrnetz anders als in den Jahrzehnten davor. Es wird vermutet, daß die in dem hochalpinen Einzugsgebiet der Quelle bereits nachgewiesene Verschlechterung der Bodenbeschaffenheit im Zusammenhang mit dem hier sehr starken Waldsterben steht. Die im Boden ablaufenden biologischen Abbau- und damit Reinigungsprozesse sind daher nicht mehr so effektiv wie früher, so daß sich diese Abbauprozesse im Rohrnetz während der Verteilung des Trinkwassers fortsetzen können. Die Ozonbehandlung des Wassers verstärkte offenbar diesen Effekt.

Die negativen Veränderungen der Umwelt scheinen somit bereits auf die Wasserversorgung durchzuschlagen. Es wird in der Zukunft eine vordringliche Aufgabe sein, die Auswirkungen der Umweltveränderungen auf das Wasser rechtzeitig zu erkennen und ihnen sachgerecht zu begegnen. Hierzu ist die Zusammenarbeit verschiedener Institutionen erforderlich.

Die Untersuchungen der Salzburger Stadtwerke ermöglichten einen Vergleich zwischen der Aufbereitung von Karstwasser durch chemisch-physikalische Verfahren und durch Untergrundpassage. Als wesentliche Erkenntnis ergibt sich, daß, zumindest für die günstigen geographischen und hydrogeologischen Verhältnisse im Grundwasserfeld Glanegg, bei der in ihrer Zusammensetzung stark wechselnden Fürstenbrunnquelle die Untergrundpassage ein

natürliches, sicheres und relativ wartungsarmes Verfahren zur Trinkwasseraufbereitung darstellt.

Die Probleme bei der Trinkwasseraufbereitung in Salzburg haben gezeigt, daß die Ozonbehandlung eines stark mit Huminstoffen belasteten Wassers nicht wie in früheren Jahren bedenkenlos eingesetzt werden kann.

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Tab. 4.2.1.: Mikrobiologische Kenndaten verschiedener Probenahmestellen aus dem Versuchsfeld Glanegg

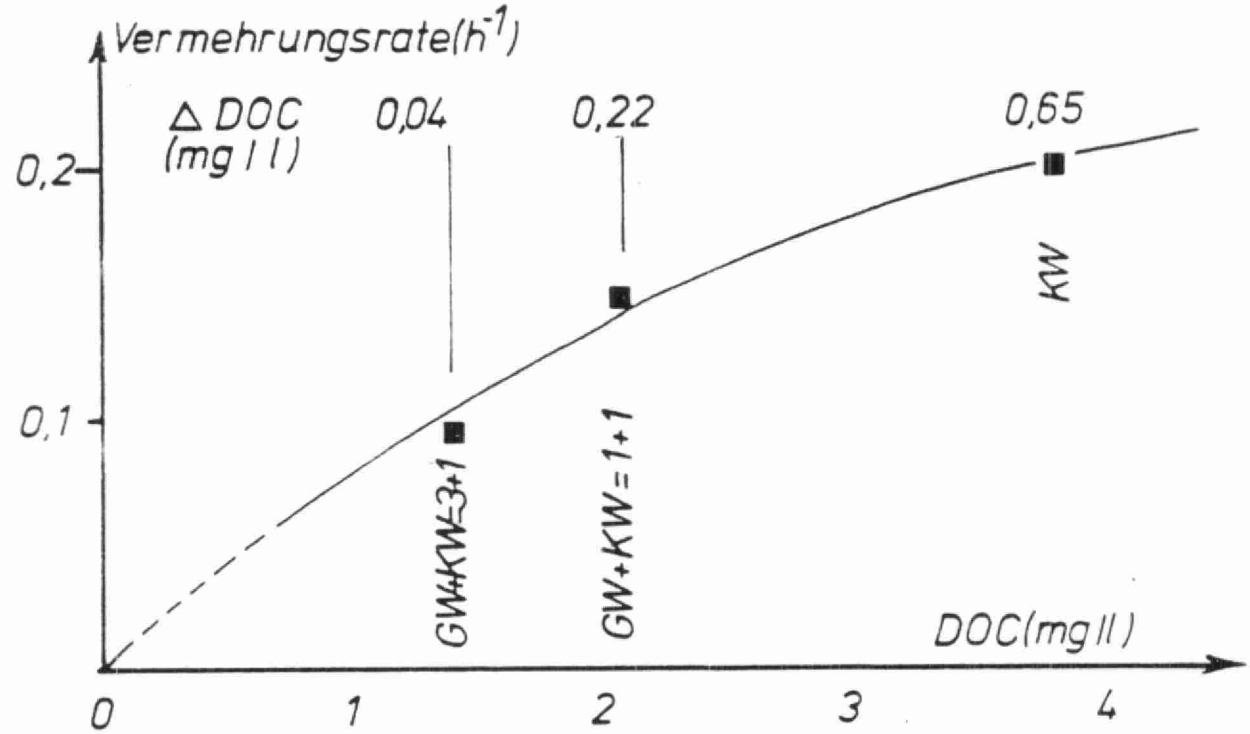
Tab. 4.2.2.: Untersuchungsergebnisse zur Vermehrungsgeschwindigkeit von Bakterien in Proben aus dem Versuchsfeld Glanegg

Probenahmestelle	Koloniezahl/ml * 20 ± 2°C 48 h	Koloniezahl/ml * 20 ± 2°C 7 Tage	Koloniezahl/ml * 36 ± 1° 48 h	Pseudomonas aeruginosa 100 ml	Gesamtzellzahl/ml (Standardabw.)	Trübungsmessung HACH 90° TEF	Trübungsmessung Monitek 12° ppm	DOC (mg/l)
Rosittenbach	37	240	305	neg.	$4,6 \times 10^4$ ($4,9 \times 10^3$)	0,16	0,55	2,21
PW Glanegg	0	0	3	neg.	$1,9 \times 10^3$ ($1,8 \times 10^3$)	0,19	1,05	0,64
P 129	2	35	13	neg.	$6,4 \times 10^3$ ($1,6 \times 10^3$)	0,46	3,50	1,89
P 130	0	0	3	neg.	$5,0 \times 10^3$ ($1,5 \times 10^3$)	0,30	1,40	1,16
P 131	0	2	39	neg.	$2,0 \times 10^4$ ($2,4 \times 10^3$)	0,29	1,60	2,17
Fürstenbrunnquelle	7	42	84	neg.	$1,6 \times 10^5$ ($1,3 \times 10^4$)	0,48	3,60	-

* Fleischextraktagar

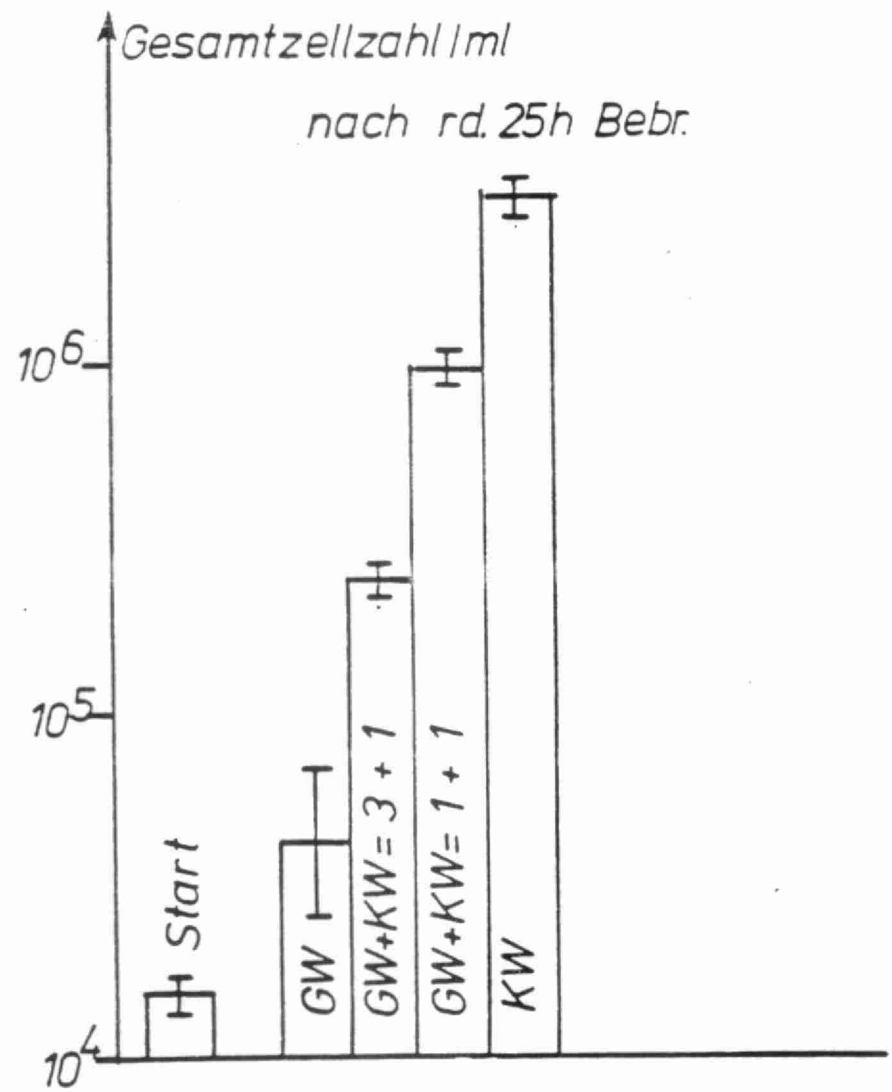
Untersuchungsergebnisse zur Vermehrungsgeschwindigkeit von Bakterien

Probenahmestelle	Vermehrungsrate	r^2	DOC (mg/l in den Ansätzen) Start	nach 52 h	nach 74 h	Gesamtzellzahl/ml in den Ansätzen Start	nach 52 h	nach 74 h
Rosittenbach	0,110	0,956	2,21	2,54	2,25	$8,5 \times 10^3$ ($8,2 \times 10^2$)	$4,3 \times 10^5$ ($4,4 \times 10^4$)	$1,5 \times 10^6$ ($3,9 \times 10^4$)
PW Glanegg	0,05	--	0,64	n.a.	n.a.	$8,5 \times 10^3$ ($8,2 \times 10^2$)	$3,0 \times 10^4$ ($4,5 \times 10^3$)	$1,6 \times 10^5$ ($2,6 \times 10^4$)
Pegel 129	0,107	0,988	1,89	2,00	1,81	$8,5 \times 10^3$ ($8,2 \times 10^2$)	$8,8 \times 10^4$ ($1,7 \times 10^4$)	$2,8 \times 10^5$ ($2,1 \times 10^4$)
Pegel 130	0,105	0,988	1,16	1,46	1,21	$8,5 \times 10^3$ ($8,2 \times 10^2$)	$6,1 \times 10^4$ ($1,2 \times 10^4$)	$2,1 \times 10^5$ ($7,3 \times 10^3$)
Pegel 131	0,112	0,988	2,17	2,07	1,92	$8,5 \times 10^3$ ($8,2 \times 10^2$)	$3,5 \times 10^5$ ($4,8 \times 10^4$)	$1,2 \times 10^6$ ($6,0 \times 10^4$)



Vermehrungsrate(h^{-1})
ΔDOC (mg/l)
0,04
0,22
0,65
0,2
0,1
KW
GW+KW=3+1
GW+KW=1+1
DOC(mg/l)
0
1
2
3
4

Abb. 3.1



Gesamtzellzahl/ml
nach rd. 25h Bebr.
10^6
10^5
10^4
Start
GW
GW+KW= 3 + 1
GW+KW= 1 + 1
KW

Abb. 3.2

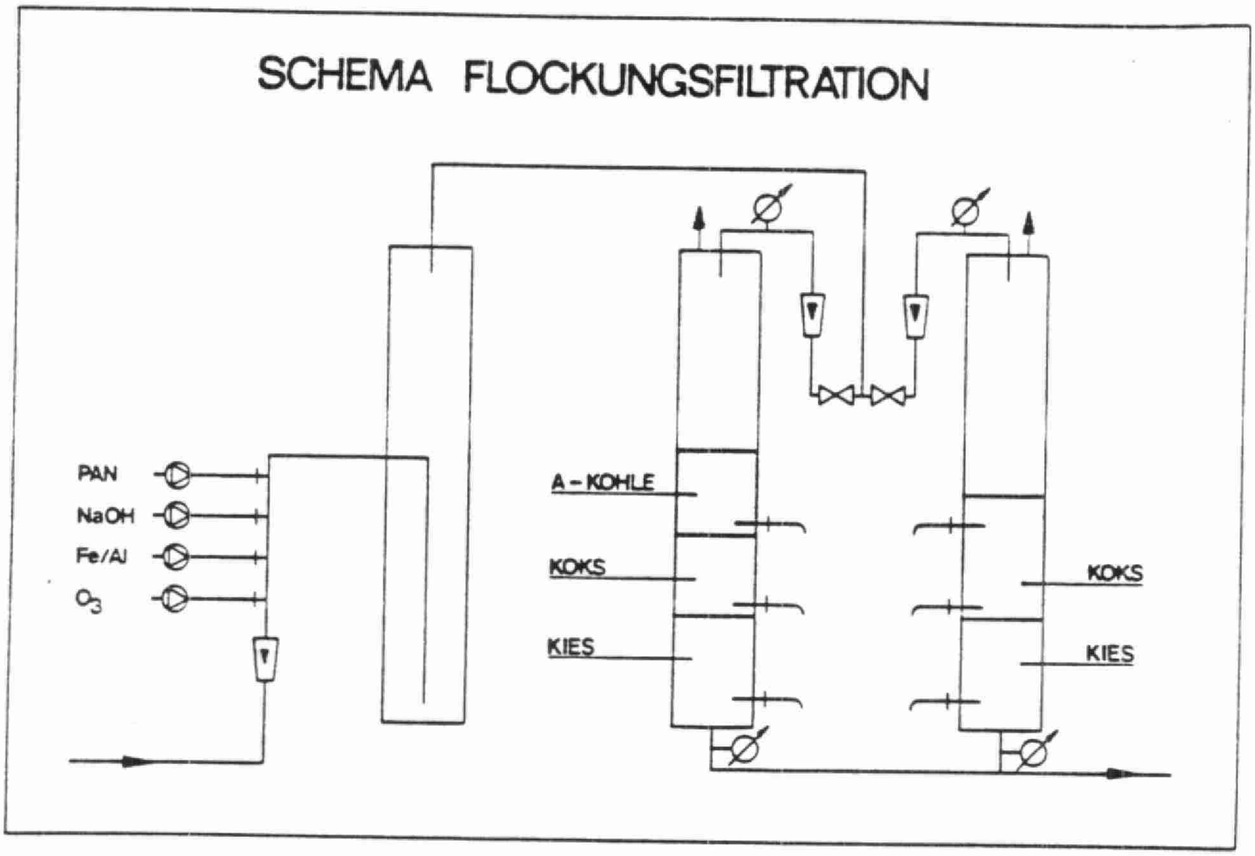

SCHEMA FLOCKUNGSFILTRATION
PAN
NaOH
Fe/Al
O_3
A-KOHLE
KOKS
KIES
KOKS
KIES

Abb. 4.1.1

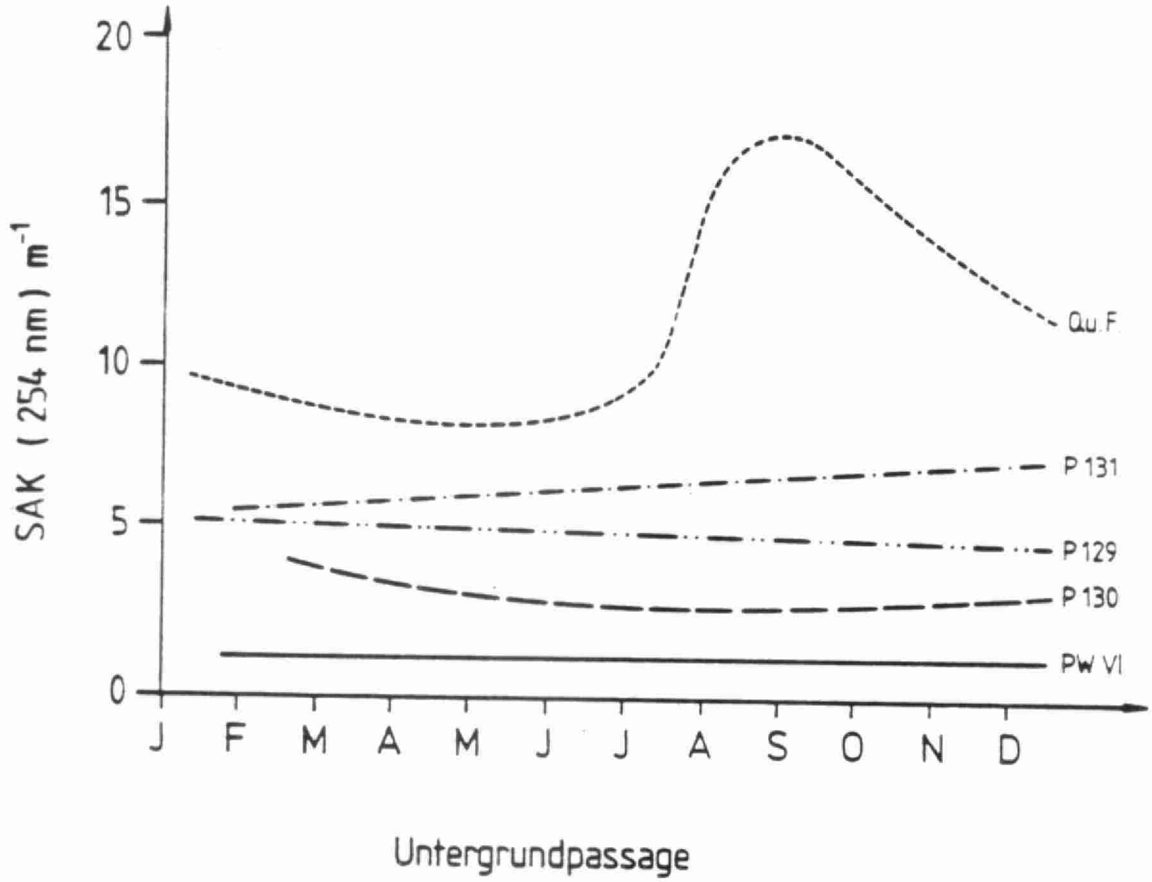
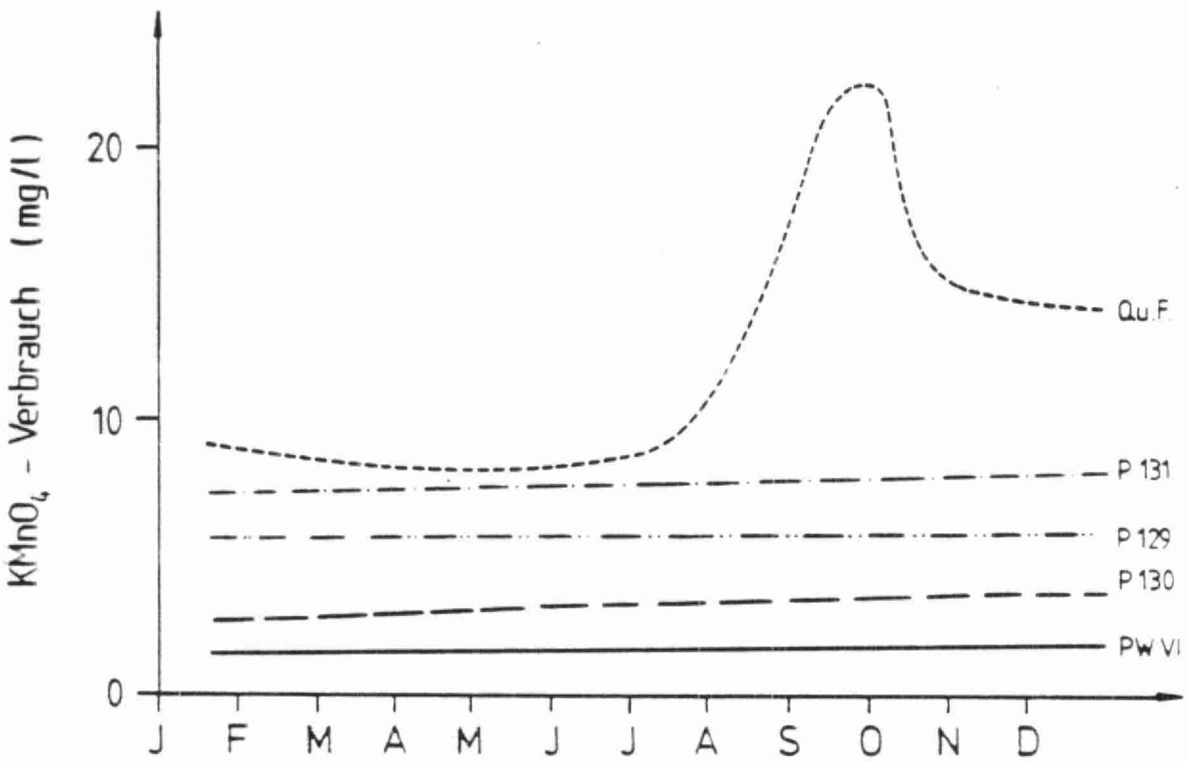
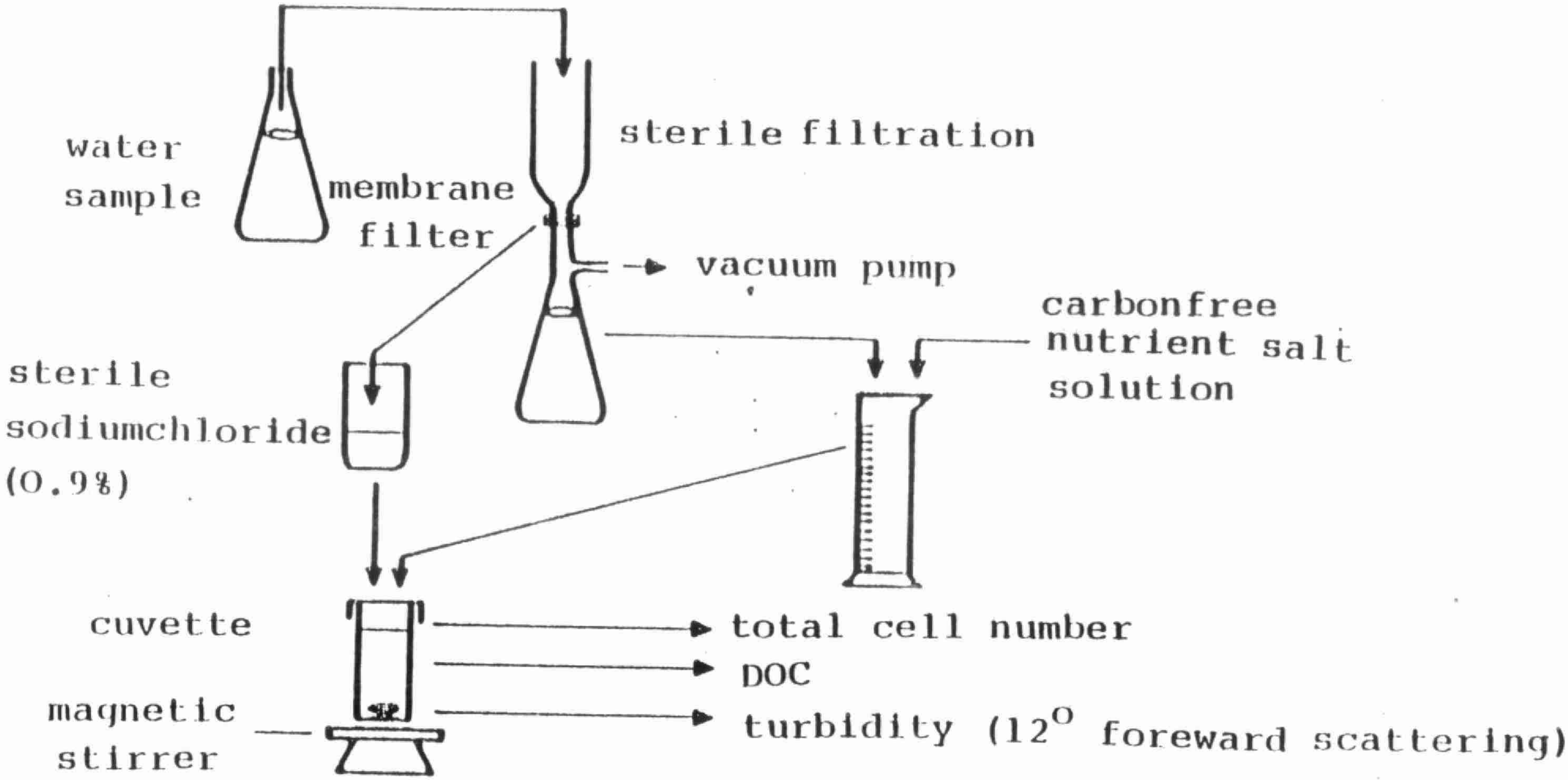

20
15
10
5
0
SAK (254 nm) m^{-1}
Qu.F.
P 131
P 129
P 130
PW VI
J
F
M
A
M
J
J
A
S
O
N
D
Untergrundpassage

Abb. 4.2.3



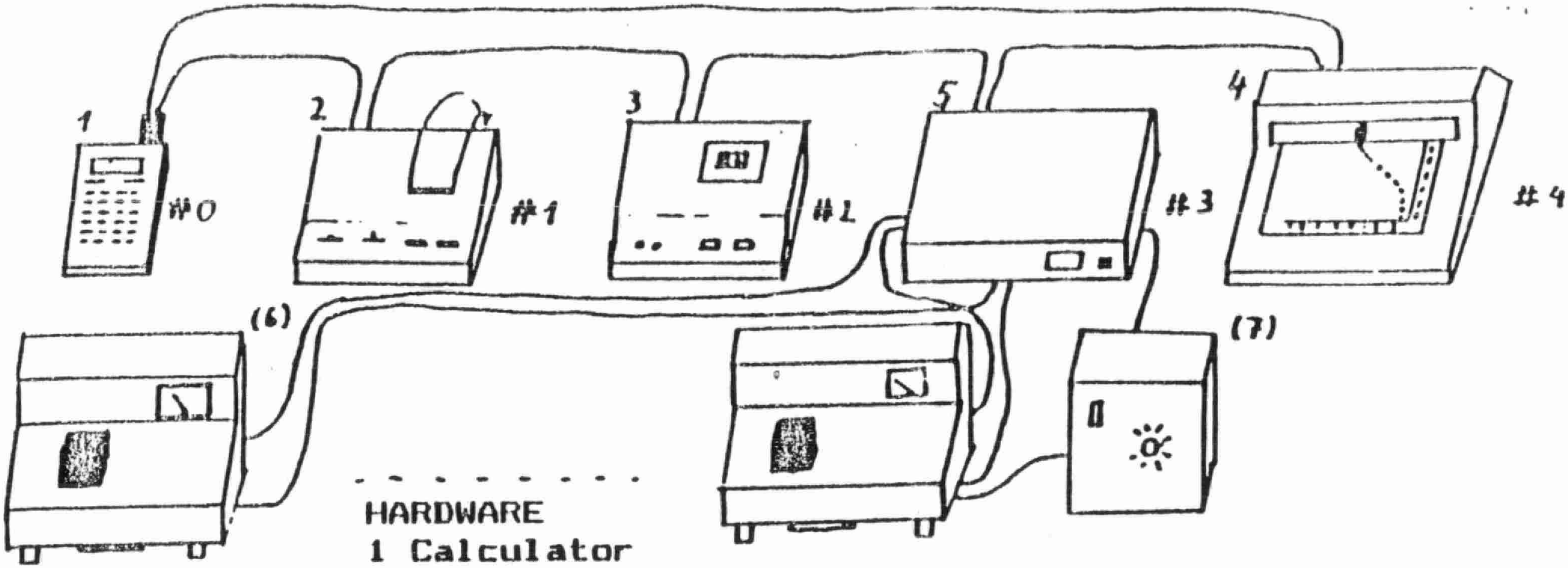
Untergrundpassage

[illegible]



WG-56

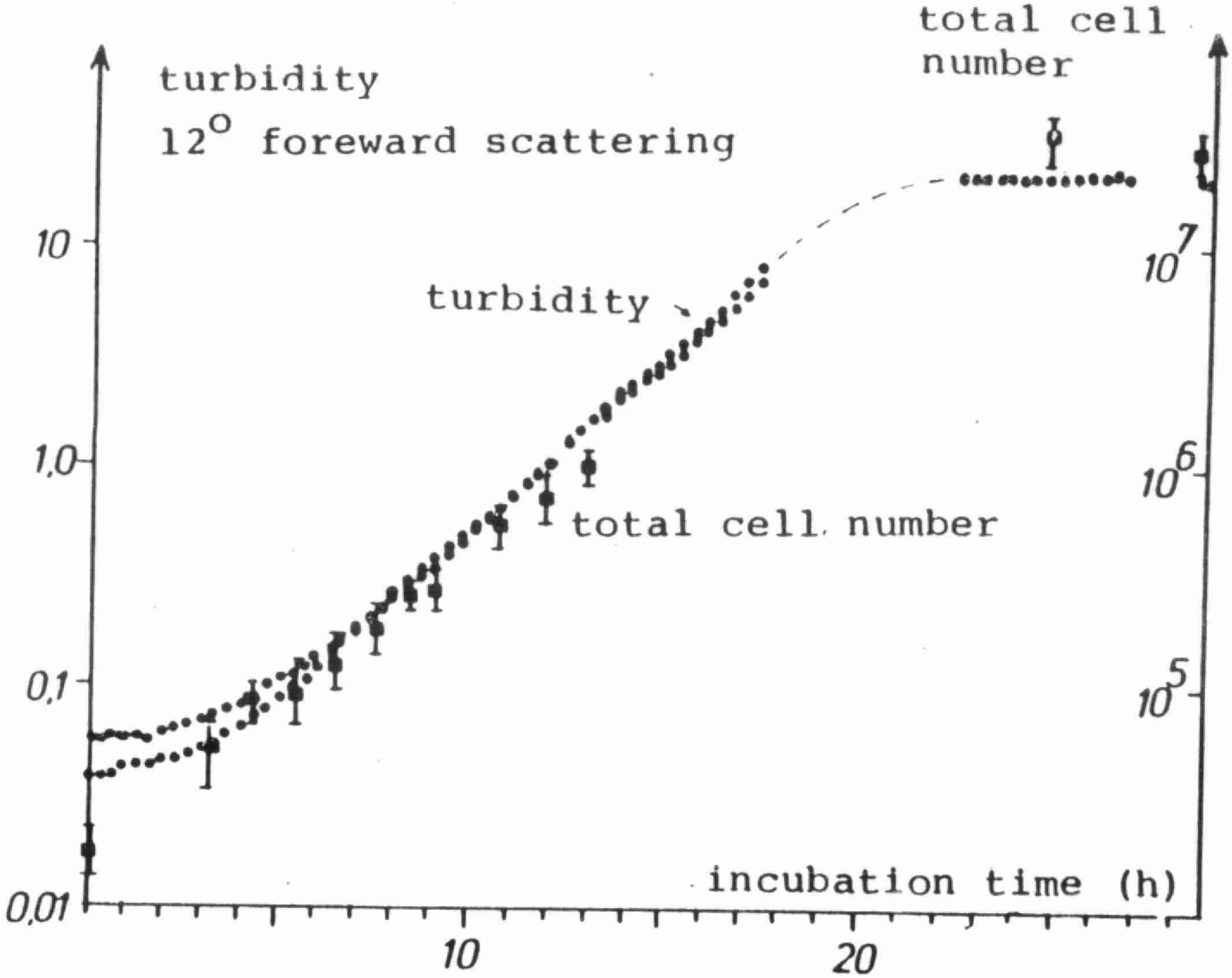
Fig 1: Preparation of the water samples for the measurement of the growth rate of bacteria



HARDWARE
1 Calculator
2 Printer
3 Cassette-Drive
4 Plotter
5 Data Acquisition and Control Unit (DACU)
6 Turbidimeters
7 Stirrers Control

WG-57

Fig 2: Automatic equipment for the turbidity measurement



WG-58

Fig 3: Multiplication of Pseudomonas fluorescens in nutrient broth, Standard deviationsas bars at the values of the total cell number

EMERGING WATER SUPPLY TECHNOLOGY AWWARF Code #: WG-04

PROJECT DESCRIPTION

Project Title:

Remediation of contaminated sites by biodegradation

Contact (name of person, organization, address, telephone):

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Project Description (Please attach a schematic diagram if appropriate):

The biodegradation of hydrocarbons by microorganisms is utilized for the remediation of contaminated sites. The method consists in optimizing the environmental conditions at the site for the mineralization processes. The conditions required are developed in the laboratory and tested in on-site and in-situ field experiments. The contaminated soil is flushed by water in which growth factors as there are ammonia and phosphates are added. A typical result of a flow-through column experiment in laboratory scale utilizing contaminated soil from a cokeovenplant is shown in the attachment.
The biodegradation is limited by the solubility of the attached hydrocarbons in the soil. The addition of inorganic solvents is tested to increase the concentration of the pollutants in the aqueous phase (see attached pre-publication). The method is still in the development and is now tested under pilot scale conditions at contaminated sites.

Operating and cost data (including data on efficiency, results, etc.):

No cost data are available, because the method was not yet applied in large scale.

Place(s) of installation/application (including dates):

The work was carried out mainly in polluted areas of cokeoven- and coal-gasification plants and of crude oil refineries. The soil is treated on-site and in-situ. See attached pre-publication.

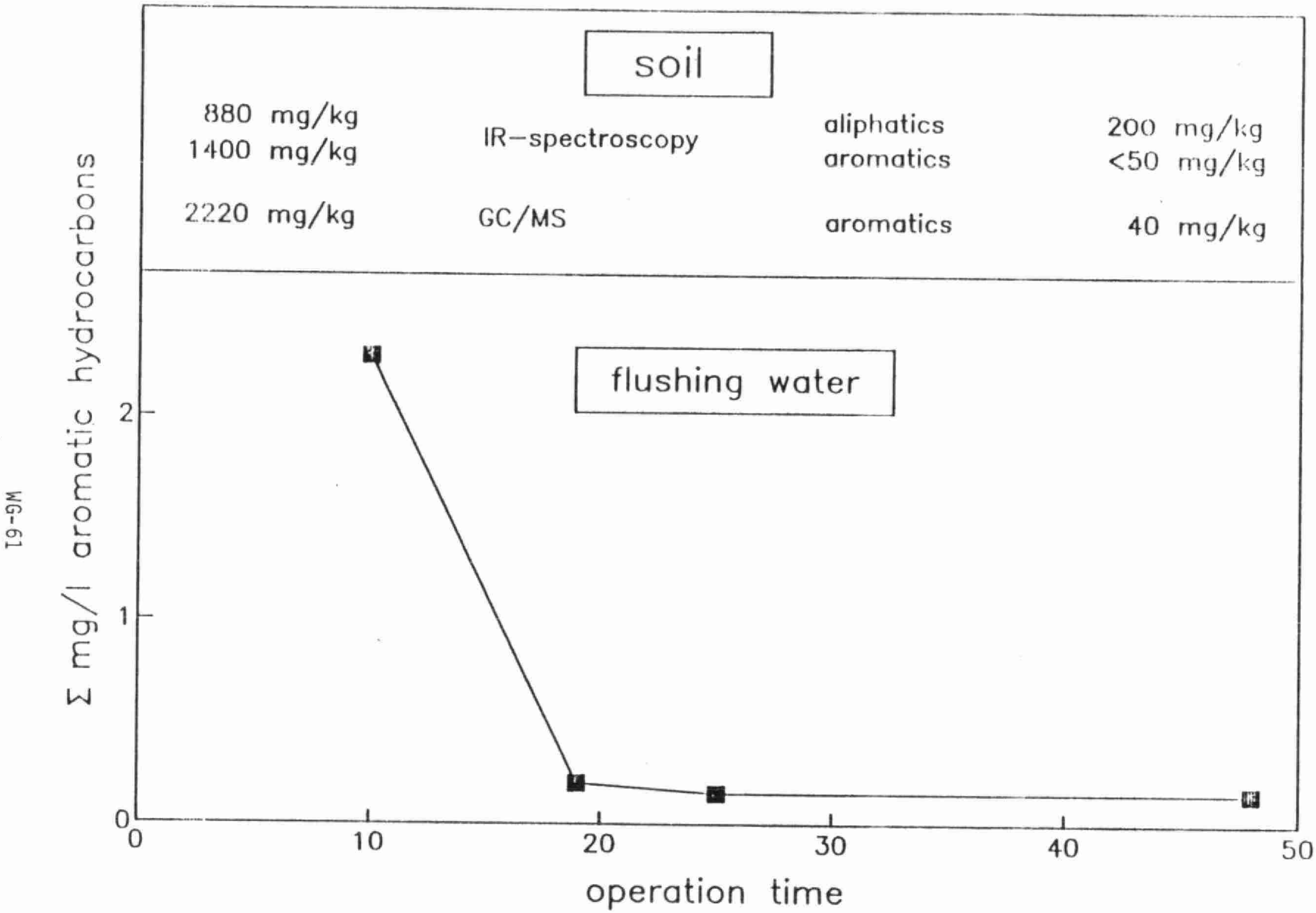
Patent staus, if applicable:

The method concerning the increase of the concentration of hydrocarbons in the aqueous phase by adding inorganic solvents is planned to be patented.

Other information (e.g., funding source, cooperating agencies, etc.):

Most of the research was sponsored by the German ministry of research and technology.

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.



Biodegradation of contaminated soil
(flow through column)

Wasserchemie Karlsruhe

1987/4324

2. Internationaler TNO/BMFT-Kongress über Altlastensanierung
Hamburg, 11.-15. April 1988

ASPECTS ON THE IN-SITU AND ON-SITE REMOVAL OF HYDROCARBONS FROM CONTAMINATED SITES BY BIODEGRADATION

P. WERNER, H.-J. BRAUCH

KEYWORDS
Behaviour (of contaminants), benzene, biodegradation, biological treatment, gas works, groundwater protection, in-situ, on-site treatment, PAH, PCA

INTRODUCTION

Biodegradation of hydrocarbons is well known since a long time (1, 2, 3). Remediation by biological methods in large scale nearby a waterplant is described by Nagel et al (4). The clean-up of a sandy aquifer polluted mainly with aromatic hydrocarbons by activating the indigenous microflora was already published by Battermann and Werner (5). The mineralization of mineraloilproducts occurs naturally worldwide, as there are to mention spills from refineries, crude oil pollution on sea and so on (3).

The processes in cokeovenplants are connected with the production of large amounts of aromatic hydrocarbons. The type of pollution consists mainly of benzene, toluene, xylene, naphthalene and polycyclic aromatic hydrocarbons (PAH's), which by permeation might endanger groundwater beneath and in the vicinity of the plants (6). Abondaned industrial areas only can be used in another way, when they are remediated. Table 1 gives an overview on the methods used for clean- up measures. The most common and classical method consists in replacing the polluted soil by non polluted one. The four first mentioned methods cannot be regarded as a final solution for the problems because the hydrocarbons are not removed and they are still existing in the environment.

TABLE 1. Remediation measures

I	Replacing the contaminated soil by non polluted one (landfill)
II	Hydraulic or mechanical prevention of spreading
III	Incapsulation
IV	Extraction
(I - IV	Contaminants are still existing)
V	Incineration
VI	Biodegradation
(V - VI	Contaminants are removed by mineralisation)

In the frame of a research programme sponsered by the German ministry for research and technology (BMFT) possibilities for the remediation of polluted industrial areas based on biodegradation in combination with physico-chemical methods supporting this process are investigated.

On-site as well as in-situ measures were tested at an abondaned coal-gasification area in North-Rhine-Westfalia in Western-Germany. The hydraulic and hydrogeological situation is described elsewhere (7). In this publication mainly the microbiological aspects are discussed.

IN-SITU TREATMENT

Three in-situ test sites were installed, which are shown as a cross section in figure 1. The penetration of the flushing water to the side was prevented by plastic layers. The soil layer below the polluted material con-

sisted in clay and showed a permeability of less than 10^{-8} m/s, which gave protection to the lower aquifers from the pollution. The sizes of the fields are given in figure 1.

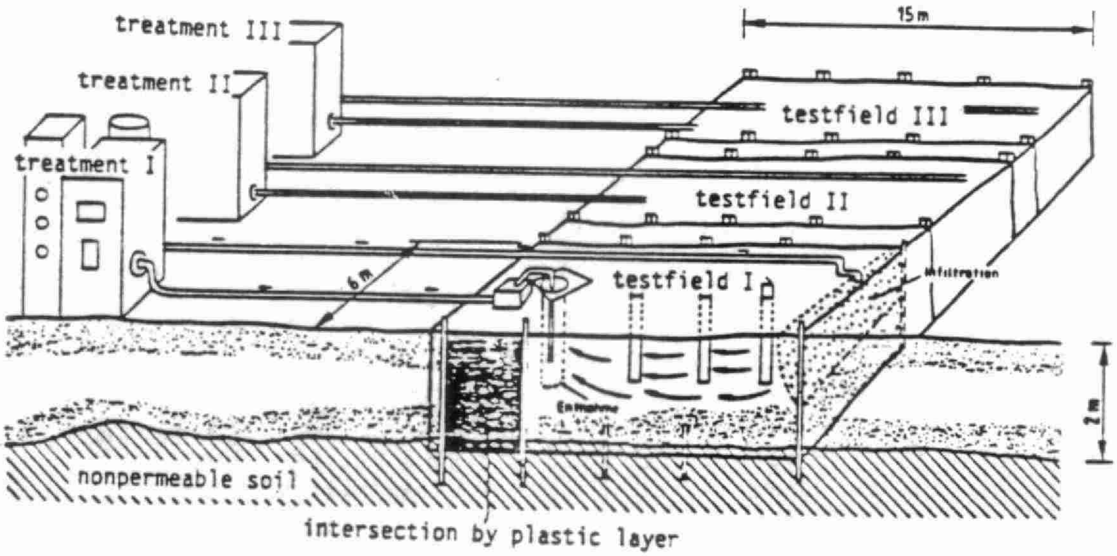


FIGURE 1. Cross-section of the in-situ test fields

The treatment of the flushing water consisted in air-stripping, flocculation, trickling and rapid sand filtration. Iron and manganese were removed and the water was aerated. In order to enhance the biodegradation nutrients as there are nitrates, ammonia and phosphates were added. The final concentration of phosphates was 0,3 mg/l and that of ammonia 1,0 mg/l. 0,5 to 1,5 m^3/h flushing water was treated, which corresponds at a porosity of 25 % to a residence time in the field experiment of 1,5 up to 3 days. A more detailed information on the treatment processes is given elsewhere (7).

The different conditions tested are listed below:

I	nutrients, H_2O_2
II	nutrients, propanol, nitrates
III	nutrients, without any additional chemicals

After an operation time of only two weeks no hydrocarbons could be detected any more in the flushing water due to their biodegradation (see below) and to their low solubility. To increase the solubility of the pollutants propanol in a final concentration of 0,5 to 1 % as a surfactant was added to the flushing water. In laboratory experiments an increase of the solubility of the soil connected hydrocarbons at the contaminated site could be found. A laboratory test was performed as follows: 50 g of polluted material was shaken in 1 l of different concentrations of methanol up to 4 % and the hydrocarbons were analysed with the help of GC/MS in the supernatant after filtration. Introducing 1 % of methanol to increase to solubility the best result was obtained. Figure 2 indicates the behaviour of 4 different hydrocarbons out of the consortia of about 20 hydrocarbons found in the polluted soil.

The use of alcohols was preferable to the majority of the other surfactants because alcohols are biodegradable and can be removed completeley even in high concentrations from the flushing water by the addition of nitrate as an electron acceptor to the system. The result of this step was as expected an increase of the concentration of the hydrocarbons in the flushing water

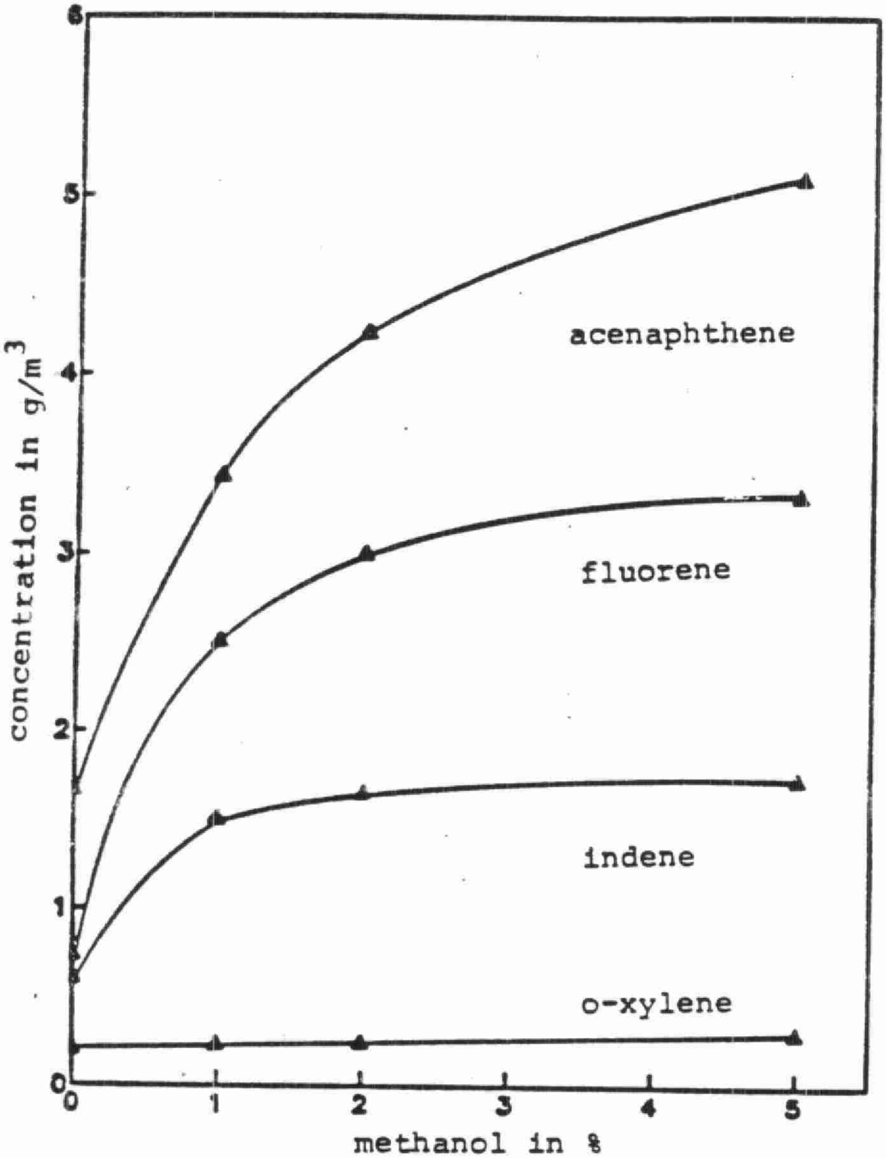


FIGURE 2.
Increase of the solubility of hydrocarbons by methanolic aqueous solutions.

(figure 3), on the other hand the permeability of the soil was lowered almost to zero, due to biomass- and gas-production. To illustrate this effect the values of acenaphthene are given. Figure 3 shows the removal of the hydrocarbons after adding the alcohols. Moreover it can be seen, that each addition of propanol was followed by a new increase of the hydrocarbons in the flushing water and their final concentrations decrease from time to time.

The removal of the dissolved hydrocarbons was due to biodegradation as could be shown in a laboratory experiment. An aliquot of flushing water from the field after the addition of alcohol was incubated in a fermenter system. Figure 4 demonstrates the mineralisation of the pollutants under aerobic conditions in the flushing water, where the propanol concentration was about 0,5 %. The sterile vial, which was poisoned by adding 100 mg/l $HgCl_2$, showed no decrease of the five analysed hydrocarbons.

In order to get more information on the influence of alcohols on the kinetics of the mineralization of hydrocarbons, the biodegradation of phenanthrene in the presence of different concentrations of propanol was investigated. An artificial test solution of phenanthrene in different concentrations of propanol up to 100 mg/l was prepared and inoculated with bacteria isolated from the flushing water of the field experiment. No influence of the propanol on the removal of the hydrocarbon could be found, as can be

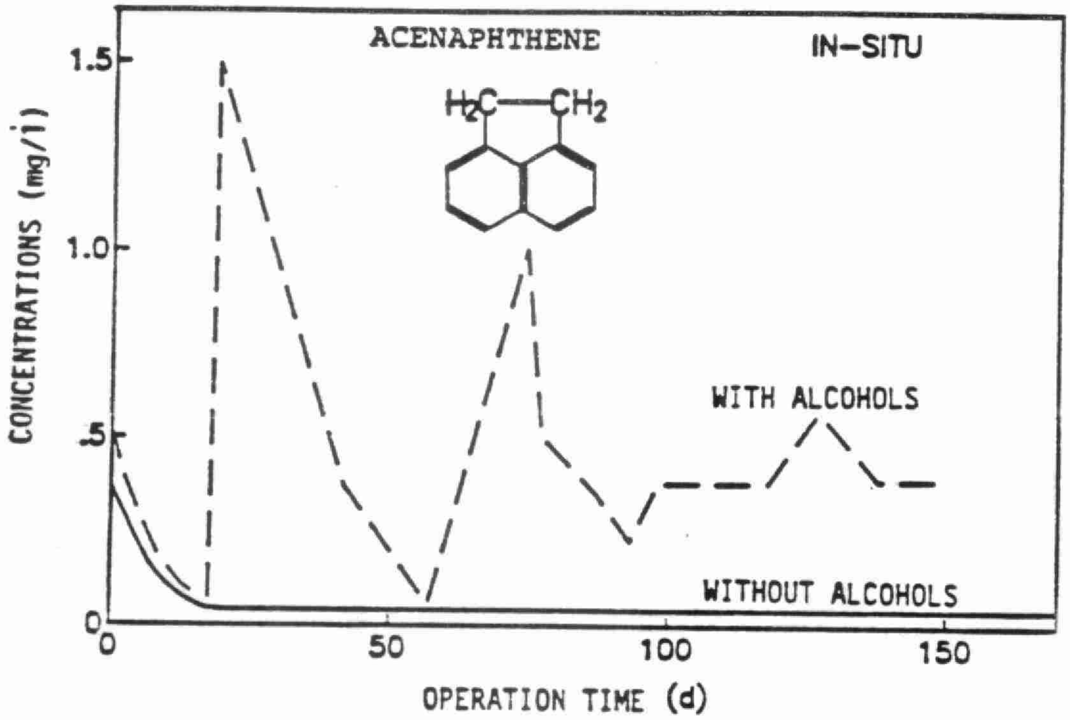


FIGURE 3. Effects of adding propanol on the solubility of hydrocarbons (Acenaphthene)

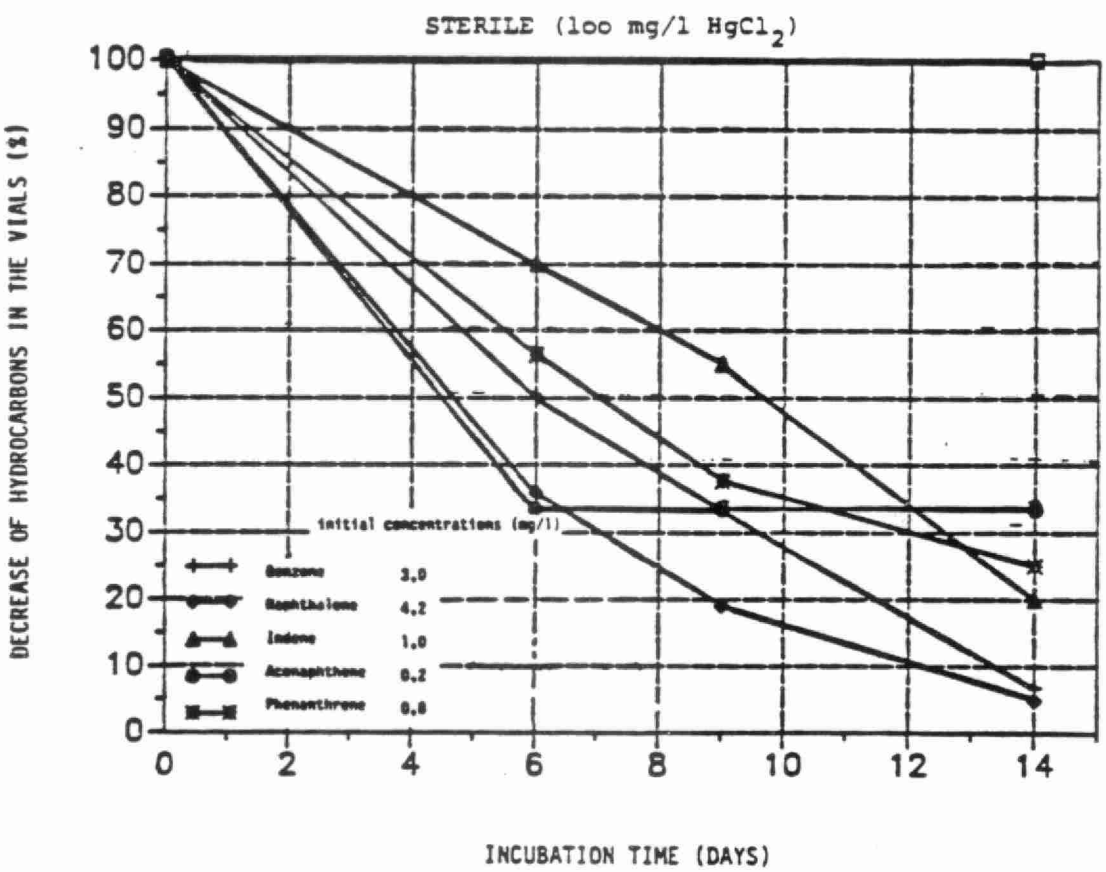


FIGURE 4. Aerobic biodegradation of hydrocarbons in flushing water in the presence of 0,5 % propanol in a laboratory test.

seen in figure 5. Although there is an increase in the bacterial counts with increasing concentrations of propanol (figure 6) no acceleration of the bio-degradation was observed.

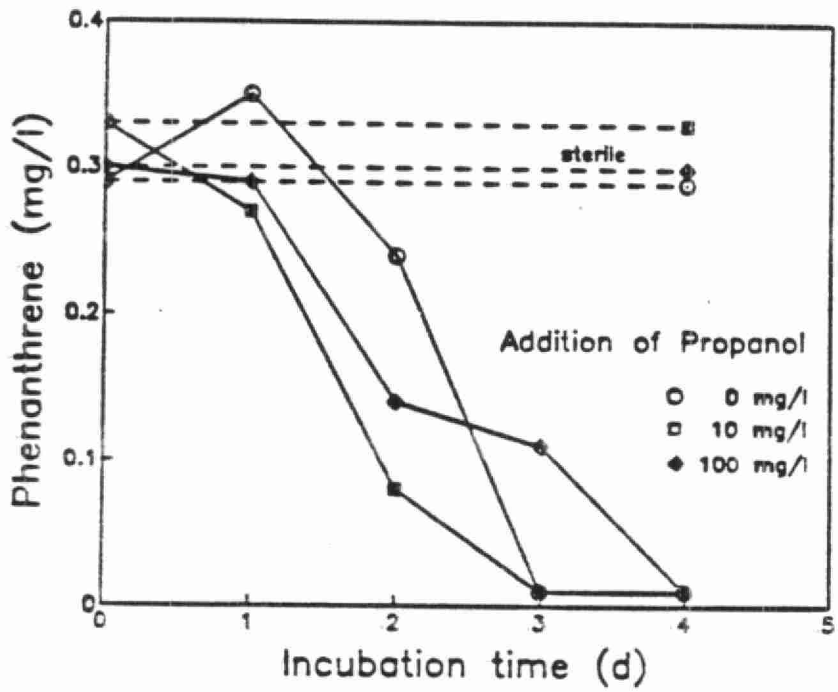


FIGURE 5. Influence of propanol on the biodegradation of phenanthrene (concentration of phenanthrene)

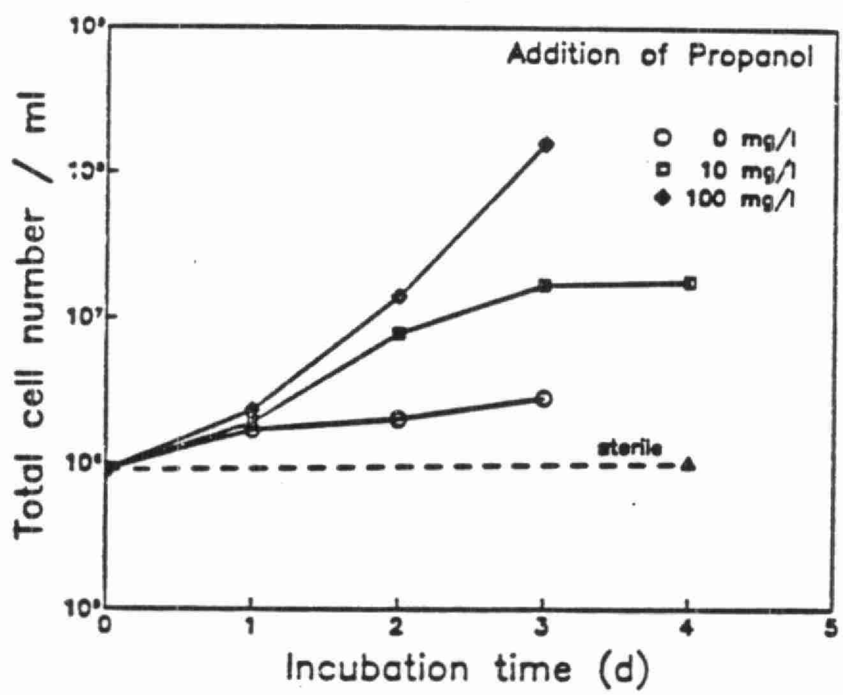


FIGURE 6. Influence of propanol on the biodegradation of phenanthrene (bacterial data)

However the data from this research remain only in the scientific and academic interest, because alcohols cannot be used in large scale neither in-situ nor on-site causing a decrease of the soil porosity due to biomass- or gas productions.

One of the main problems concerning remediation methods in-situ is the inhomogeneity of the polluted soil. The distribution of the flushing water was not at all homogenious and therefore parts of the contaminated site could not be flushed by the water. Although the biodegradation of the hydrocarbons was excellent as shown above, in-situ treatment seems not to be promising as a clean up process. After an operation time of about 1 year in all three experimental sites still high concentrations of hydrocarbons in the soil could be detected, being in the same range as at the beginning (about 1 g/kg soil), while at the same time the flushing water was already free of contaminants.

The optimum requirements for in-situ treatment are listed in table 2. If all of these requirements are met, the in-situ measures would be possible, but for the most cases an on-site treatment seems to be preferable.

TABLE 2. Requirements for biological in-situ-treatment

MICROBIOLOGICAL POINTS OF VIEW:

BIODEGRADABILITY OF THE CONTAMINANTS
CONCENTRATION OF THE CONTAMINANTS
ABSENCE OF TOXIC SUBSTANCES (E.G. HEAVY METALS)
SOLUBILITY OF THE CONTAMINANTS

HYDROGEOLOGICAL POINTS OF VIEW:

HYDRAULIC CONDUCTIVITY 5×10^{-4} M/S
FLUSHING CIRCUIT
WATER TREATMENT BEFORE INFILTRATION
HOMOGENIOUS DISTRIBUTION OF THE CONTAMINANTS
PREVENTION OF SPREADING OF THE CONTAMINANTS
HOMOGENIOUS FLUSHING THROUGH THE CONTAMINATED SOIL

BIODEGRADATION TESTS IN LABORATORY SCALE

These investigations were performed in order to obtain more information on the conditions required for the on-site treatment of polluted soils. The biodegradation tests of hydrocarbon polluted soil were performed in percolation devices. The sample was filled in a 1 m long column with a diameter of 10 cm. The soil was flushed downstream continuously using about 30 l of tap water to which nutrients as there are ammonia and phosphates were added. Because the permeability of the soil flushed differed, a by-pass had been installed. The possibility to inject oxygen is given. Several sample taps allow to observe the waterquality during the run.

The results from an experiment with soil from an abondaned coalgasification plant are shown in figures 7 and 8. After 2 weeks of operation time no hydrocarbons in the flushing water could be detected, although the DOC-value was still very high (about 50 mg/l). The initial concentration of hydrocarbons in the soil measured by IR-spectroscopy was 1400 mg/kg aromatic and 800 mg/kg aliphatic compounds. They decreased in the course of an operation time of about 50 days to less than 200 mg/kg aromatic hydrocarbons and aliphatic compounds were lower than detection limit. Utilizing GC/MS analysis similar results could be obtained. The initial concentration of coke-

ovenplant specific substances of 2200 mg/kg as a sum was biodegraded to 40 mg/kg (figure 8). The bacterial counts indicate decreasing values with decreasing contents of hydrocarbons. The initial colony counts in the flushing water were in a range of more than 10^6 /ml and after an operation time of 40 days less than 10^4 /ml could be found.

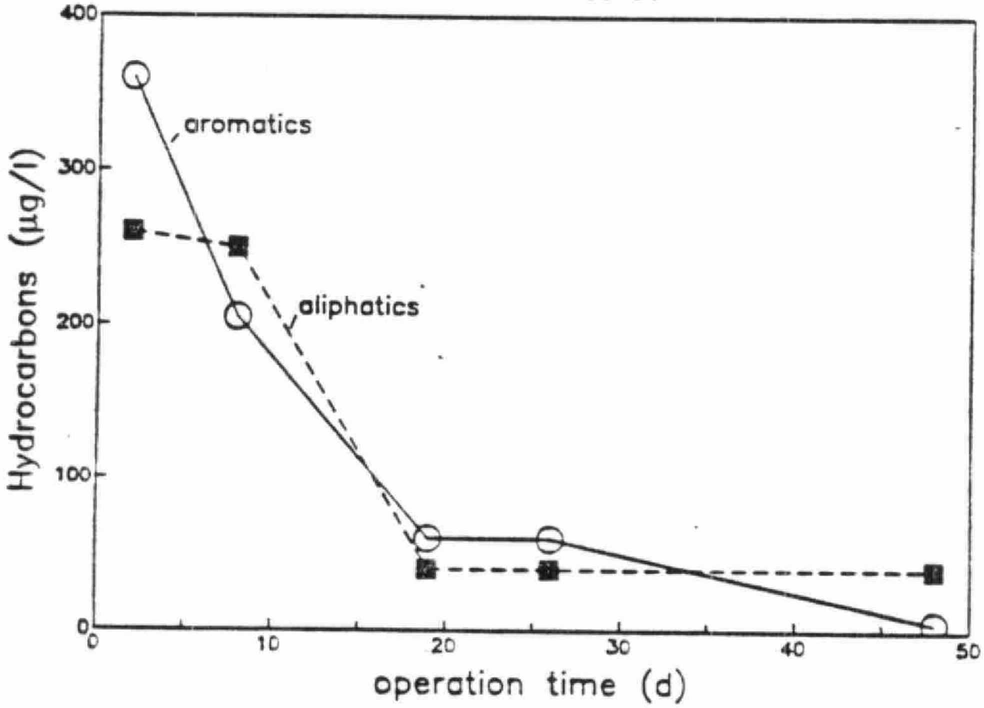


FIGURE 7. Biodegradation of hydrocarbons in a flow-through column filled with contaminated soil - hydrocarbons in the flushing water

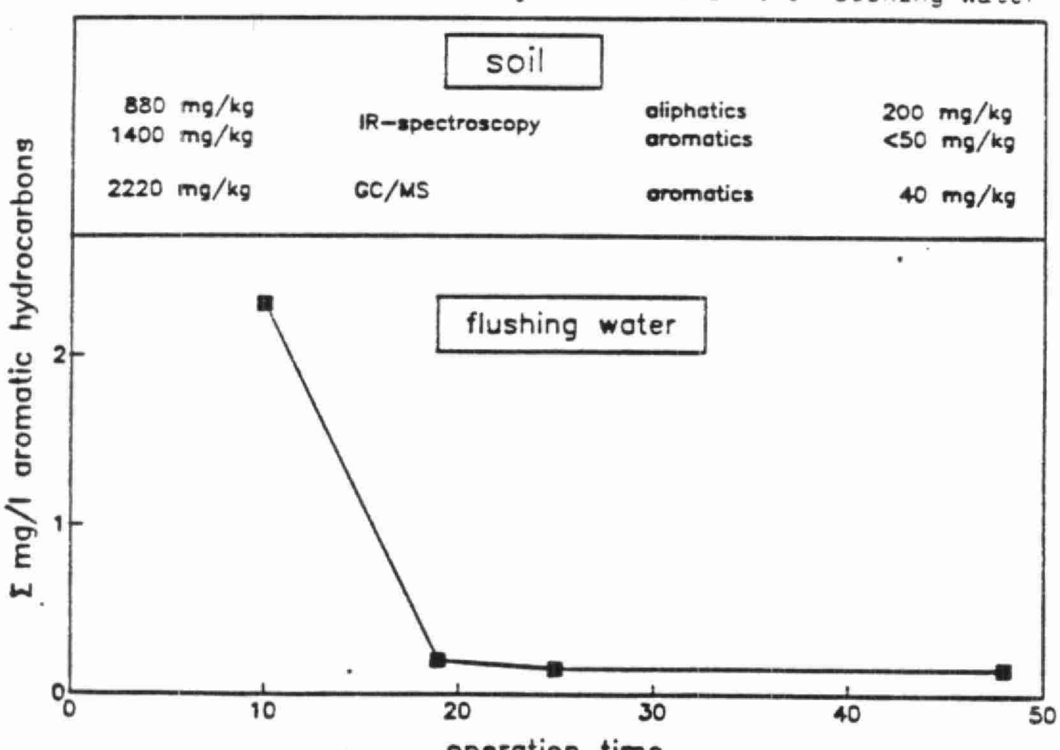


FIGURE 8. Biodegradation of hydrocarbons in a flow-through column filled with contaminated soil - hydrocarbons in the soil and the flushing water

In another experiment the column was filled with soil from the same coke-ovenplant with similar initial concentrations of hydrocarbons in the soil (about 2200 mg/kg). The run was performed as described above. In this case the concentration of the pollutants in the flushing water was about one order of magnitude higher than in the run mentioned earlier (figure 9). A rapid decrease of the concentration of hydrocarbons in the water measured by infraredspectroscopy was found. After an operation time of 5 months about 75 % of the polluting compounds in the soil analyzed by GC/MS were biodegraded (table 3).

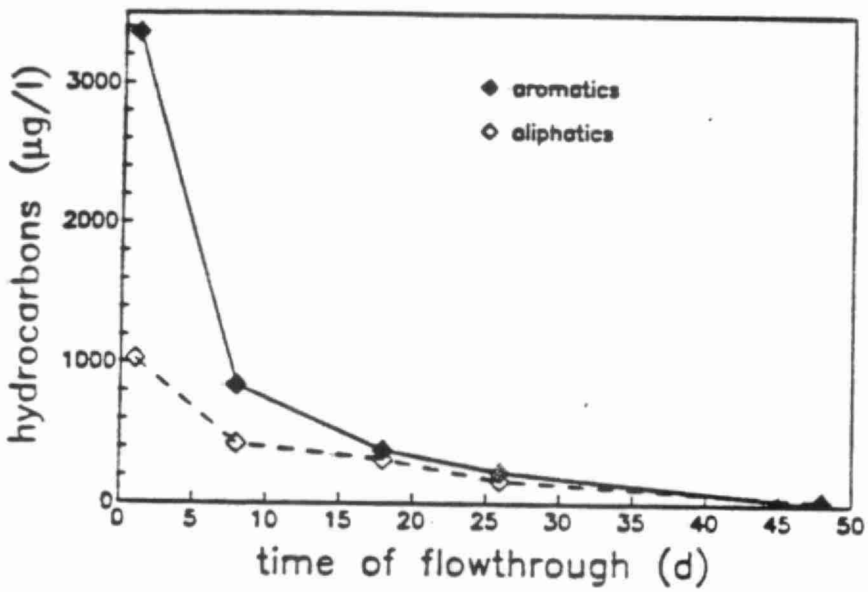


FIGURE 9. Biodegradation of hydrocarbons in a flow-through column filled with contaminated soil - hydrocarbons in the flushing water

TABLE 3. Concentration of hydrocarbons in soil before and after microbial remediation in a flow-through column

concentrations in mg/kg	initial	after 5 months	decrease (%)
Indene	5,5	1,7	69 %
Indan	5,1	0,25	95 %
Naphthalene	59	11	81 %
1-Methylnaphthalene	87	14	84 %
2-Methylnaphthalene	112	10	91 %
Acenaphthene	187	26	86 %
Acenaphthylene	29	7,4	74 %
1,1-Biphenyl	31	7,3	76 %
Fluorene	245	71	71 %
Anthracene	130	41	68 %
Phenanthrene	277	134	52 %
Pyrene	285	31	89 %
Fluoranthene	430	111	74 %
Chrysene	135	37	73 %
Benz[a] anthracene	200	96	66 %

The data of the laboratory and field experiments can serve as indications for the practical applicability of such measures concerning on-site treatment. At the mentioned abondaned coalgasification plant 3 on-site test

fields were installed. The tests are not yet completed and the results shall be published in a future publication.

MOBILIZATION OF THE CONTAMINANTS

The experience from the experiments show that the removal of hydrocarbons in contaminated sites is limited by the adhesion of the pollutants to the soil. As discussed earlier it was not worthwhile to try to overcome the problem by utilizing alcohols as surfactants, because this step causes clogging of the soil. Therefore other methods must be developed to bring the contaminants in satisfactory contact to the bacteria. One possibility could be to decrease the adsorbability of the hydrocarbons to the soil. Hydrocarbons are highly adsorbed especially by clay materials.

In our experiments an inorganic substance was used to increase the concentration of the hydrocarbons in the aqueous phase by releasing them from the clay.

Figure 10 shows an example of the benificial effect of utilizing this method. A contaminated soil from an abondaned coalgasification plant (1 g hydrocarbons/kg soil) was brought into contact with different aqueous concentrations of this substance and shaken for about 1 hour. While in pure water only a very small amount of the hydrocarbons were dissolved the values increased to 8 mg/l hydrocarbons at a final solvent concentration of 0,5 % (submitted as a patent). The results received show that this substance is nontoxic and does not serve as a substrate for the bacteria as alcohols do. Moreover it can be removed by flocculation afterwards.

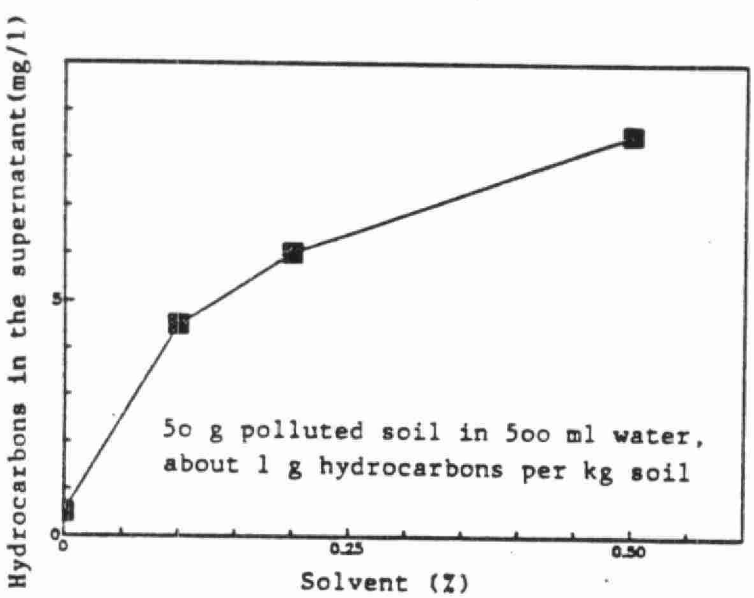


FIGURE 10. Effect of an inorganic solvent on the mobilisation of hydrocarbons from contaminated soil.

It is planned to characterize the behaviour of such solvents and to test their applicability for remediation measures in the frame of future research projects.

In conclusion we can say that the biodegradation of hydrocarbons itself is not the only problem. Moreover the use of microbial activity for remediation methods needs further research on the optimum conditions required for the mineralization. In addition it is necessary to bring the contaminants in a close contact with the bacteria to enable the biodegradation.

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EMERGING WATER SUPPLY TECHNOLOGY AWWARF Code #: WG-05

PROJECT DESCRIPTION

Project Title:

Preparation of $Ca(OH)_2$ solution for water softening

Contact (name of person, organization, address, telephone):

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Postfach 6 65, D-7000 Stuttgart 1
Tel.: 0711-21751

Project Description (Please attach a schematic diagram if appropriate):

Lime softening can be used with larger success, if the lime is given in solution. In this case it will also be possible to use the calcium carbonate as a powder for paper making etc. But 15 - 30 % of the water to be treated has to be used for preparing this clear solution. The apparatus to do this can be reduced in size through a high energy dissolution lank with short retention time followed by a lamella separator. More details can be seen from the attached schematic diagram.

Operating and cost data (including data on efficiency, results, etc.):

One advantage can be seen in the possibility to use cheap lime qualities and the lacking necessity of a prefiltration of the $Ca(OH)_2$ solution.

Place(s) of installation/application (including dates):

Zweckverband Landeswasserversorgung
Wasserwerk Langenau

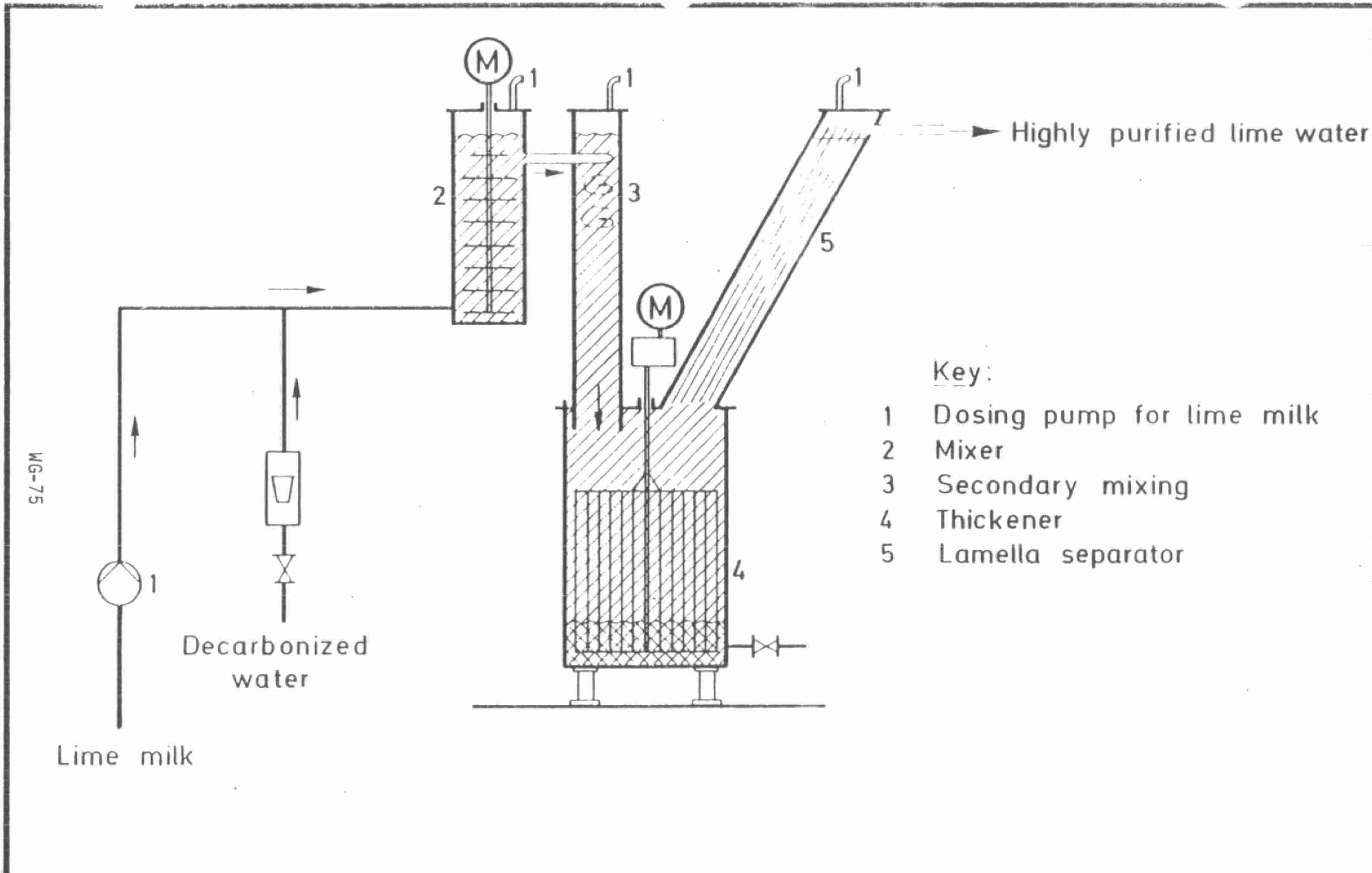
Patent staus, if applicable:

Patent applied.

Other information (e.g., funding source, cooperating agencies, etc.):

Publication:
Flinspach, D.; Werner, G.: Recovery of High-Purity Calcium Carbonate during the Decarbonization of Drinking Water. Aqua, No. 1/1987 Pergamon Journals Limited IWSA 003-7214/87

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.



NEW TYPE OF SYSTEM FOR THE PREPARATION OF HIGHLY PURIFIED LIME WATER

FIGURE 3
Ö86.808

Aqua No. 1, pp. 45 to 49, 1987
Printed in Great Britain

0003-7214/87 $3.00 + .00
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IWSA

Recovery of High-Purity Calcium Carbonate during the Decarbonization of Drinking Water

D. Flinspach and G. Werner, *Zweckverband Landeswasserversorgung Stuttgart, Schützenstraße 4, D-7000 Stuttgart, FRG*

Abstract: The Landeswasserversorgung Stuttgart (Stuttgart Regional Water Supply Association) has developed a new type of decarbonization system which is significantly more compact, efficient and reliable in service than previously known plants of this kind. In this context, it is especially important that the new type of system provides for the recovery of calcium carbonate in an ultrapure, industrially usable form during the decarbonization of drinking water. The sale of high-grade calcium carbonate solves the disposal problems and contributes to covering the operating costs of decarbonization. In order to recover calcium carbonate of ultrapure quality, it proved necessary to use repurified lime water instead of lime milk; the former is produced applying a method which has likewise been developed recently.

La récupération d'un carbonate de calcium de grande pureté pendant la décarburation de l'eau potable

Résumé: La Landeswasserversorgung Stuttgart (Association de Distribution d'Eau de la Région de Stuttgart) a mis au point un nouveau système de décarburation qui est sensiblement plus ramassé, plus efficace et plus fiable que les installations de cette nature précédemment connues. Elément très important, ce nouveau système permet de récupérer le carbonate de calcium sous une forme ultra pure et industriellement utilisable au cours de la décarburation de l'eau potable. La vente de carbonate de calcium de haute qualité résout les problèmes d'évacuation et contribue à couvrir les dépenses d'exploitation du procédé. Afin d'obtenir du carbonate de calcium d'une qualité ultra pure, il est nécessaire d'utiliser de l'eau de chaux au lieu du lait de chaux; le premier est produit en appliquant une méthode qui a été également récemment mise au point.

Introduction

The Landeswasserversorgung Stuttgart (Stuttgart Regional Water Supply Association) is one of the largest and oldest long-distance supply systems in the Federal Republic of Germany. The enterprise was formed in 1912 and at present supplies water to 2.5 million inhabitants of 220 cities and communities in southern Germany (Baden-Württemberg), including the city of Stuttgart and its environs. In 1985, the drinking water supplied amounted to 85 M m^3.

Because water is scarce in the area supplied by the Landeswasserversorgung Stuttgart, the water must be obtained in the catchment area of the Danube between Ulm and Heidenheim. From here three long-distance pipelines are used to transport the drinking water over a distance of 100 km to the area of greatest demand, Stuttgart and its environs (Fig. 1).

In the region between Ulm and Heidenheim, the Landeswasserversorgung Stuttgart operates three groundwater purification plants and one surface-water treatment plant in which river water from the Danube is treated to produce drinking water. Approximately 70 M m^3 of water is obtained annually from the groundwater plants and approximately 15 M m^3 from the Danube water treatment plant (Langenau Waterworks), although the capacity of the latter is approximately 70 M m^3/yr.

The hardness of the water obtained in the individual waterworks varies considerably. Whereas the hardness of the groundwater has values between 3.1 and 5.0 mol/m^3, the hard-

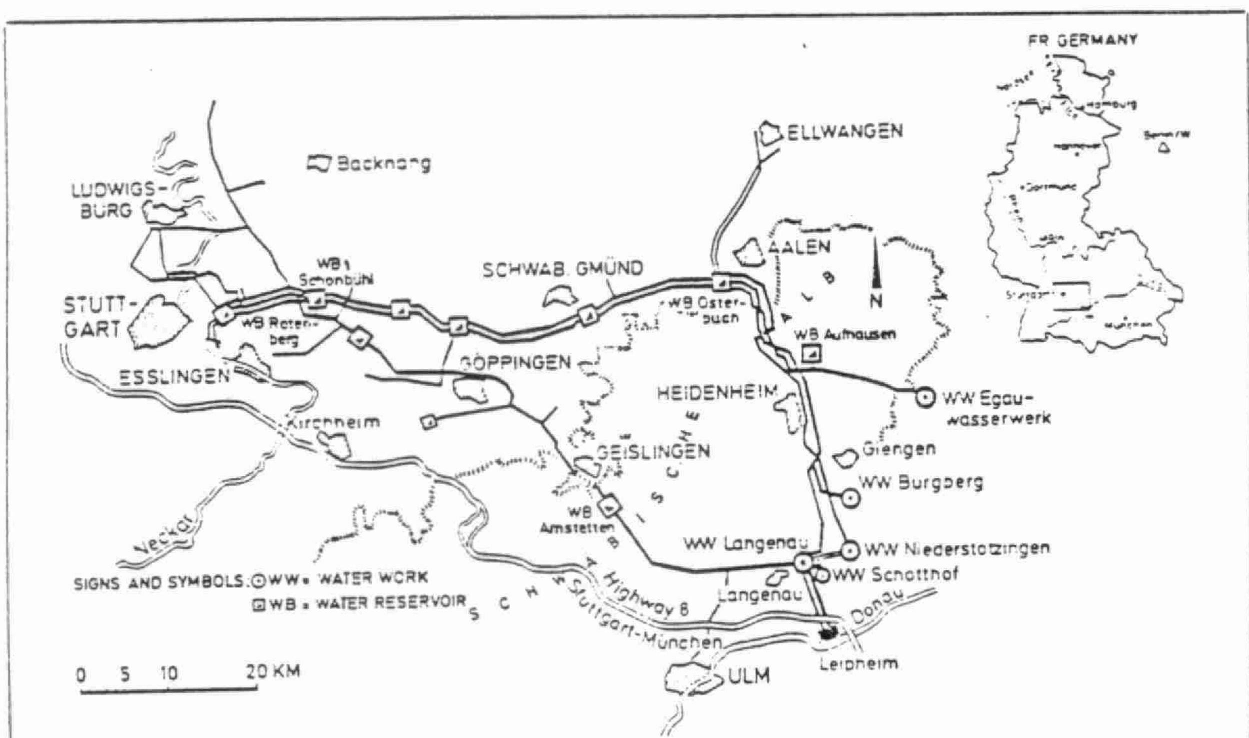

Fig. 1. Location map showing plants and area served by the Landeswasserversorgung Stuttgart

ness of the Danube water is about 2.5 mol/m^3. The drinking water supplied is a mixture of the water obtained in the individual waterworks and has a hardness of approximately 3.6 mol/m^3.

The drinking water of the Landeswasserversorgung Stuttgart is to be classified as especially high-grade with respect to its properties as a foodstuff and does not have to be softened for this purpose. For some time, however, it has been noticeable that the consumers' desire for softer drinking water has been growing, and water softeners are being installed increasingly in residential buildings. The resulting costs for the consumer are considerable, and the technical maintenance and hygienic conditions of such installations present certain difficulties.

For this reason, the Landeswasserversorgung Stuttgart decided to investigate how the hardness of the water could be reduced to some extent. The obvious solution to this problem was to decarbonize the hard groundwater and to remix it with the other water. The objective is to reduce the hardness of the drinking water from 3.6 mol/m^3 to approximately 2.5 mol/m^3.

High-purity calcium carbonate as an interesting raw material for further industrial utilization

Various technically perfected methods are available for the central softening of drinking water. For the project of the Landeswasserversorgung Stuttgart, however, it became evident at an early point that for technical and economic reasons only a decarbonization processs using hydrated lime could be considered.[1] The decisive factor in this context was that the compact flocculation system commissioned in the Langenau Waterworks in 1981 can be used for such a process. This system was developed and constructed by the Landeswasserversorgung Stuttgart to improve the treatment of river water from the Danube.[2] It is designed as a two-line system: each line has a flow rate capacity of 750 l/s. Except for periods of extremely high consumption, the capacity of a single line is adequate for Danube water treatment so that normally the second line is available for other purposes. Comprehensive investigations have shown that the compact flocculation system is outstandingly suitable for use in carrying out a type of "accelerated slow decarbonization". This new type of decarbonization process is characterized by the following advantages in particular:

- The special design of the compact flocculation system provides for problem-free operation with very high concentrations of contact sludge, e.g. up to more than 15 kg/m^3 of the groundwater to be decarbonized.
- For this reason, the decarbonization process is always completed although the reaction time of less than 10 min is short by comparison with conventional slow decarbonization plants. The total detention time in the installation, including separation of solids amounts to just under 20 min.
- Thanks to the special design of the thickener with a lamella separator, the precipitated calcium carbonate and the contact sludge are retained almost completely so that the filters are hardly loaded. The solids content in the effluent can be kept lower than 1–2 mg/l.

Although this means that the prerequisites for a central softening process were favorable in the Langenau Waterworks, one obstacle still remained, i.e. the disposal of the calcium carbonate sludge produced during the decarbonization process. It must be noted that at least 14,500 t/yr. of calcium carbonate, calculated as dry solid matter, result from the planned decarbonization process. Because the calcium carbonate is obtained as sludge with a solids content of approximately 30–35%, this results in the problem of disposing of 130 t of excess sludge daily.

Table 1 shows the reaction equation for the decarbonization process and the associated mass balance. Moreover, it must be noted that in addition to the removal of the calcium hydrogen carbonate ($Ca(HCO_3)_2$) the free carbon dioxide contained in the groundwater — amounting to 60 g/m^3 in the case of the Landeswasserversorgung Stuttgart — must be bounded.

Table 1. Decarbonization –CA(OH)$_2$ Demand – CACO$_3$ Yield

Objective	Specific demand for $Ca(OH)_2$	Specific yield: $CaCO_3$
Reduction of water hardness by 1mol/m^3	74 g/m^3	200 g/m^3
Removal of 1 g CO_2 / m^3	1.7 g/m^3	2.27 g/m^3

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O$$

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$$

These data make it clear that in the final analysis the planned decarbonization process is a problem of lime sludge removal. For both technical and economic reasons, a process of sludge deposition leads to almost insuperable difficulties because suitable sludge dumping areas of the required magnitude are not available in the large zones for the protection of water encircling the Langenau Waterworks. A good solution could therefore be found only if the calcium carbonate sludge could be successfully passed on for further utilization.

The search for a sales market led to the recognition that calcium carbonate is in fact a raw material which can be used in large amounts, for example, in the plastics, dyestuff and in particular the paper industries. The prerequisite for an economically interesting market is, however, that the material be offered to the purchasers concerned in an ultrapure form, above all with a high degree of whiteness.

The groundwater of the regional water supply system is naturally very pure and in particular contains no significant iron and manganese impurities so the purity requirements of the calcium carbonate can be satisfied in this respect. Difficulties arose, however, with respect to the calcium hydroxide or calcium oxide to be used as precipitants. All the technical products available on the market exhibit such high impurities that the resulting precipitated calcium carbonate is unsuitable for further utilization.

Problems with the recovery of superpure industrially usable calcium carbonate during the decarbonization process

In the spring of 1982, the Federal Minister for Research and Technology (BMFT) gave its approval to the Landeswasserversorgung Stuttgart to implement a research project in order to develop the methodological bases for a groundwater decarbonization process in which high-purity calcium carbonate is produced. This project has been concluded in the meantime.

In a second stage, the process developed in recent years by the Landeswasserversorgung Stuttgart is to be implemented in practice, likewise in the context of a research project, in which the prototype of an industrial-scale plant for groundwater decarbonization is to be planned and erected. According to the current time schedule, such a large-scale plant will be commissioned in the Langenau Waterworks around the beginning of 1989.

The following discussion describes the problems faced by the research project and the manner in which they were solved.

The first problem was to secure the envisaged high-purity of the calcium carbonate which could not be achieved using the hydrated lime available on the market. It was first attempted to recalcinate the carbonate produced during decarbonization operation in high-grade steel reactors using electrical energy in order to attain a pure calcium oxide which can in turn be used as precipitant. It was soon evident, however, that this method

could not be used for reasons of cost. The subsequent efforts concentrated on the purification of industrial hydrated lime.

This approach resulted in a practical solution to the problem if lime water is used instead of lime milk for the decarbonization process, for impurities can be separated more easily from lime water than from lime milk. The system for the production of highly purified lime water is shown in Fig. 2.

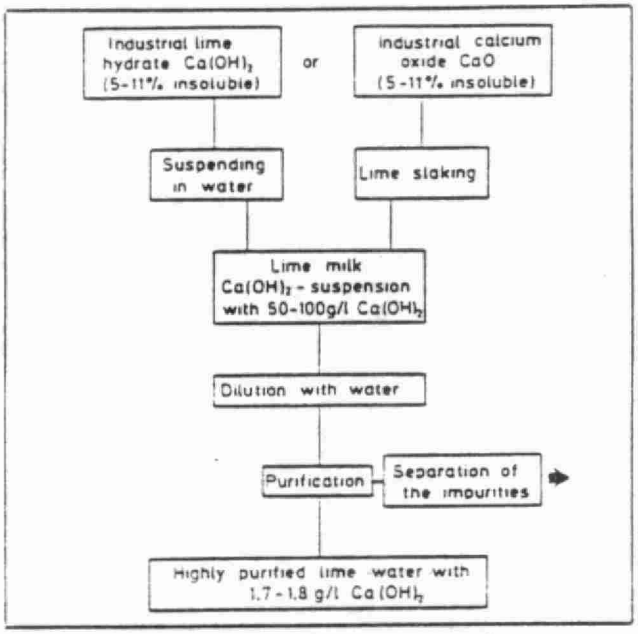

Fig. 2. Schematic diagram of the lime water preparation system

Lime water is normally produced in lime saturators in which fresh water is fed from below into a fluidized bed composed of hydrated lime, and lime water is drawn off at the top. These conventional reactors must be very large because they can work at very low upflow velocities. Moreover, they are sensitive to flow-rate fluctuations and also exhibit a number of other disadvantages which makes them appear to be unsuitable for continuous production of relatively large amounts of lime water. These disadvantages are avoided by a lime water preparation system newly developed by the Landeswasserversorgung Stuttgart shown in Fig. 3. Using this system, the several hours previously required for the detention period in the reactor can be reduced to approximately 10 min.

After lime milk and decarbonated water are mixed intensively for a short period in a stirring tank, the mixture is introduced into a final reaction tank. In the latter, the magnesium still present in the decarbonized dissolving water, assisted by the high pH value, forms a highly settleable floc, which occludes the insoluble impurities of the hydrated lime. The floc formation process is augmented additionally by traces of a coagulent aid. Finally, the lime water with the flocs is fed to a thickener in which a lamella separator is incorporated. The purified lime water flows out of the latter to the actual decarbonization stage.

As described above, the decarbonization process itself takes place on a line of the existing compact flocculation system (Fig. 4). This is implemented as follows: the precipitation process is initiated by mixing the groundwater to be decarbonized with the highly purified lime water in the first reaction chamber. At the same time concentrated calcium carbonate sludge is returned from the thickener and mixed intensively using the stirring devices in chambers Ia and Ib. By this means, the calcium carbonate precipitated in this process can accumulate to the contact sludge. Finally, a coagulant aid is added in reaction chamber III in order to improve the settling characteristics of the calcium carbonate. In this way large flocs are formed in the subsequent chamber IV, and they can be separated without difficulty in the thickener of the compact flocculation system. The outflowing, decarbonized groundwater has an extremely low solids content and hardly loads the filters.

A new problem emerged, however, from tests on a semi-industrial system (flow rate: 16 m^3/hr): the high-purity calcium carbonate precipitated using lime water has an outstanding tendency to crystallize. During the first decarbonization experiments performed using lime milk, the average diameter of the particles of the calcium carbonate sludge did not exceed 15 — 20 µm (50% value). When lime water was used however, they grew within a few days to a diameter of approximately 150 µm. The result was that the sludge in the thickener was dense to such a great degree that it could no longer be pumped, stored and transported. The solution to this problem was ultimately provided by wet-grinding the sludge. Different types of mills were tested to discover which was the most suitable: in this context it should be noted that such mills require a relatively large amount of energy for operation. The many studies performed showed that the high-purity calcium carbonate sludge should have an average grain diameter of 6–8 µm. Such a sludge can still be pumped and transported without difficulty.

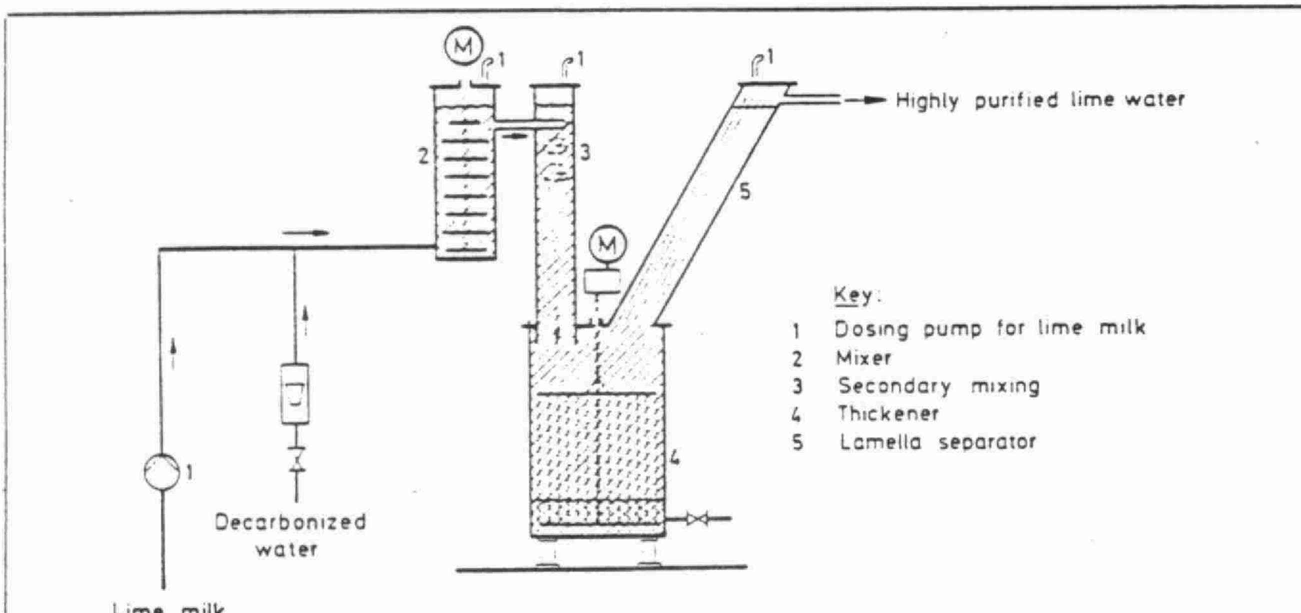

Fig. 3. New type of system for the preparation of highly purified lime water

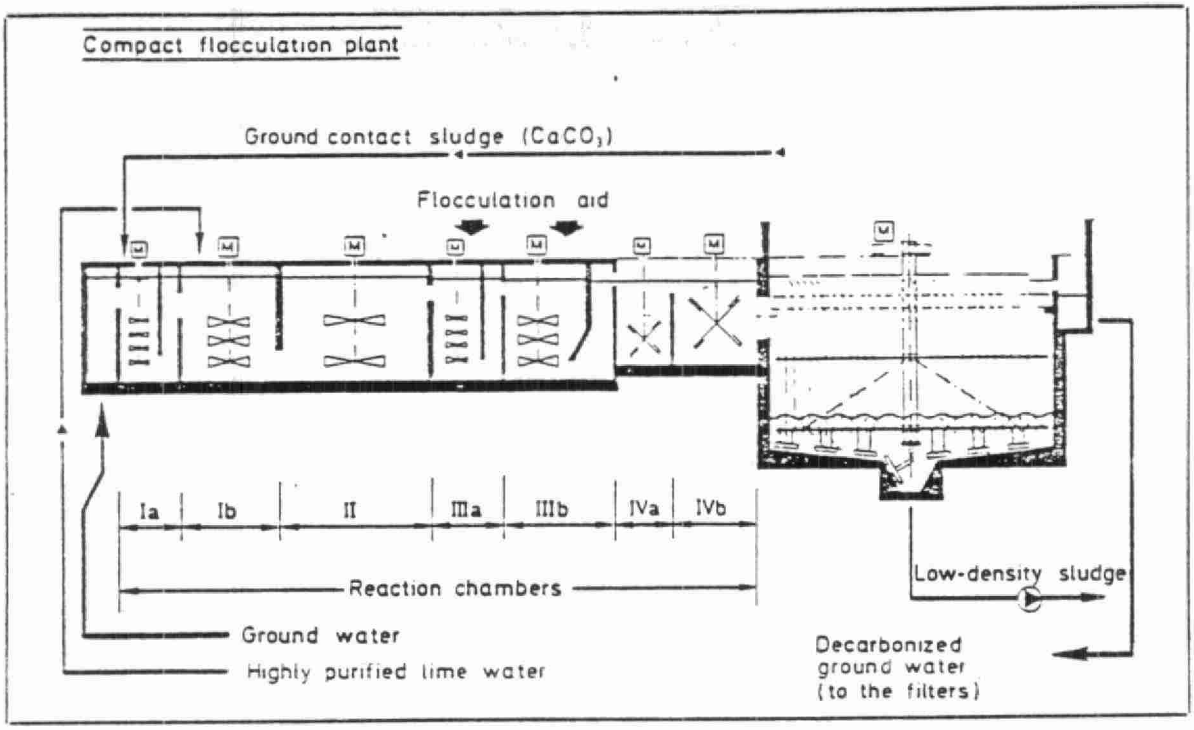

Fig. 4. Compact flocculation system in decarbonization operation

In addition, it proved to be the case that a so-called stirring ball mill can be considered as the most suitable for wet grinding. Here the grinding process is effected by glass or ceramic beads which are moved by an agitator.

Finally, a third problem remained to be solved, i.e. the concentration of the sludge. The solids content of the sludge developed in the thickener of the compact flocculation system is approximately 30–35% by weight. This concentration must be raised to approximately 65% for transport to the purchaser and for further industrial utilization. In other words, about 650 kg of calcium carbonate must be contained as a dry substance in one metric tonne of sludge. Subsequent studies have shown in the meantime that the desired concentration can best be achieved by using centrifuges.

The newly developed process for groundwater decarbonization with recovery of high-purity calcium carbonate

Based on the comprehensive preliminary investigations and the subsequent research results, the Landeswasserversorgung Stuttgart has now developed a practicable process for groundwater decarbonization with recovery of high-purity calcium carbonate. A system in which this process can be implemented on an industrial scale is subdivided into the following process stages:

1. Storage of calcium oxide or calcium hydroxide, metering and preparation of lime milk;
2. Lime water preparation;
3. Decarbonization in the compact flocculation system;
4. Use of ball mills to grind the contact sludge conducted in the circuit;
5. Storage of thin sludge;
6. Concentration of the calcium carbonate sludge;
7. Stocking and loading of the thickened slurry to be transported.

Figure 5 provides a schematic diagram of the system, which has been perfected technically in the meantime and is currently being implemented in the Langenau Waterworks. It is designed for a groundwater flow of up to 650 l/s and the carbonate hardness (6.4 mol/m^3) is removed almost completely.

This fully decarbonized partial flow is then mixed with water which has not been decarbonized so that the resulting mixture has the desired hardness of 2.5 mol/m^3. The compact flocculation system is the only existing equipment for the eight process stages listed; all other components must be provided as new items. The additional costs are estimated at 12 million DM.

The present calculation for the operating costs proceed from the assumption that approximately 600.000 DM/yr. must be spent for power and approximately 600.000 DM/yr. for calcium oxide and coagulant aids. These costs are covered by the sale of the highly purified calcium carbonate. The remaining costs for personnel, maintenance, repairs and depreciation will raise the price of water from the Landeswasserversorgung Stuttgart by approximately 0.015 DM/m^3 given annual delivery of 85 million m^3/yr.

Conclusions

The research project described here is trailblazing in several respects. First of all, it is a model for analogous systems for the decarbonization of drinking water in which the further industrial utilization of the high-purity calcium carbonate produced is to be viewed not only in terms of the recovery of a raw material and environmental protection but also from an economic point of view. In addition, it is to be anticipated that the project's individual system sections will provide impulses for other development work. This applies, for example, to the decarbonization of process water in industry.

The use of the compact flocculation system, designed originally for the treatment of surface water, as a high-rate decarbonization plant is in itself an important innovation. Even if the recovery of high-purity calcium carbonate is not a primary consideration, this method can be used, for example, to construct inexpensive, compact decarbonization plants of high efficiency which will in many cases not require any subsequent filtration of the decarbonized water.

A similar claim can be made for the newly developed process for the preparation of highly purified lime water, which can be used for all projects in which large amounts of lime water must be provided continuously. One relevant field of application, for example, is the use of lime water in the operation of water works if the binding of excess, free carbon dioxide is an important concern or if the water is to be hardened.

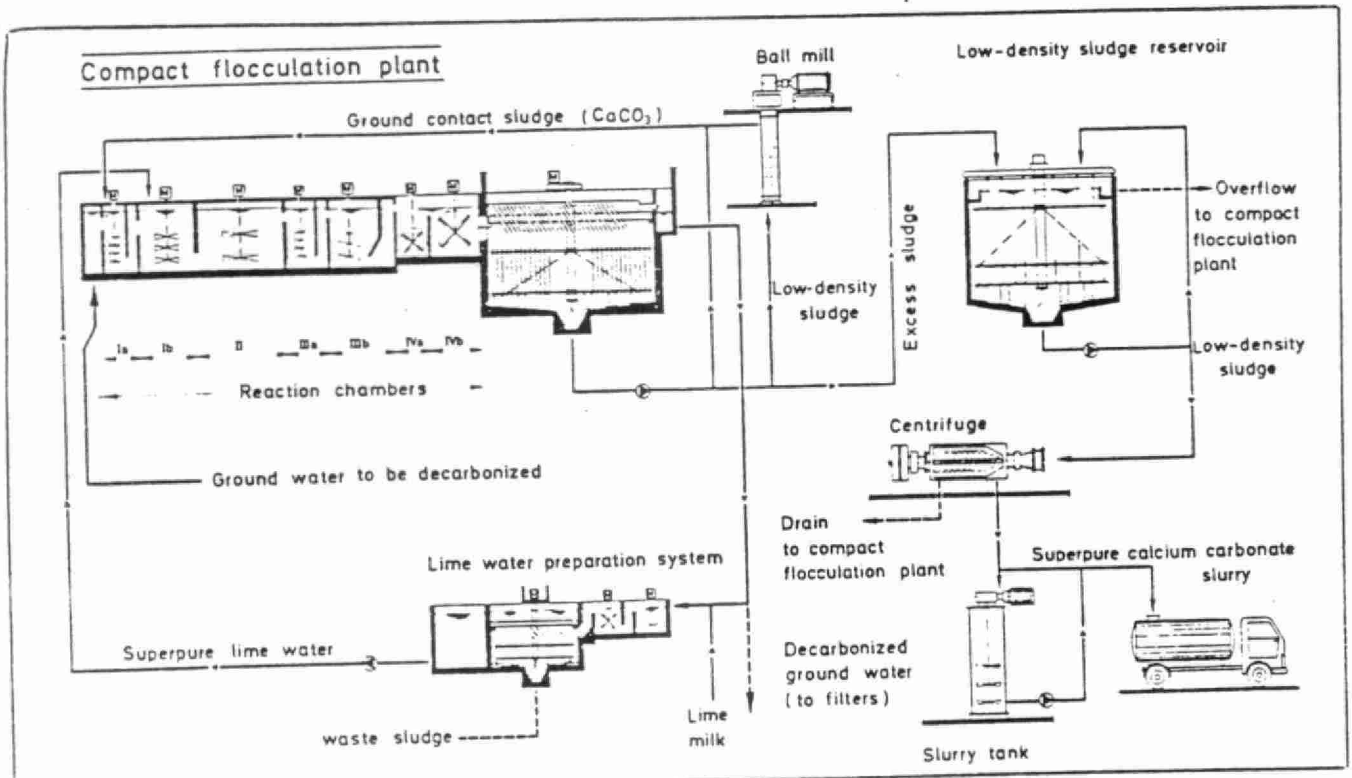

Fig. 5. Process diagram for groundwater decarbonization with recovery of high-purity calcium carbonate

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2. Wölfel, P., Werner, G. and Flinspach, D. The new compact flocculation system of the Landeswasserversorgung Stuttgart — development, erection, possible applications and operating experience, *DVGW-Shriftenreihe Wasser* No. 104, ZfGW, Frankfurt (1982) (in German).

PROJECT DESCRIPTION

Project Title:

Biological Denitrifikation Process with Hydrogen-Oxidizing Bacteria for Drinking Water Treatment

Contact (name of person, organization, address, telephone):

Dipl. Ing. Gerhard Schnoor
Sulzer Anlagen- und Gebäudetechnik GmbH
POB 380 D-6308 Butzbach W.-Germany
Telex: 4184484 Phone: 06033-8910 Fax: 06033-891 139

Project Description (Please attach a schematic diagram if appropriate):

Development status : full-scale use
since June 87 water supply use

It is a biological process in which nitrate is selectively eliminated.
Nitrogen gas is liberated during the process but no inorganic concentrates or salt solutions are produced;
The substrate used (= nutrient for the microorganisms) is hydrogen which is completely harmless to potable water;
In contrast to other substrates as methanol, ethanol or acetic acid etc., no further steps are needed to remove excess substrate;
The conditions in the biological reactor are so selective, that only a few species of specific microorganisms can survive and develop;
The reproduction rate (production of excess biomass) is desirably very low and only minimal amounts of biomass need to be disposed of;
The technical side of the plant is extremely simple and robust. Process management is stable and reliable.

Operating and cost data (including data on efficiency, results, etc.):

Please see attached papers

Place(s) of installation/application (including dates):

Stadtwerke Mönchengladbach GmbH
Voltastrasse 2
D-4050 Mönchengladbach 1

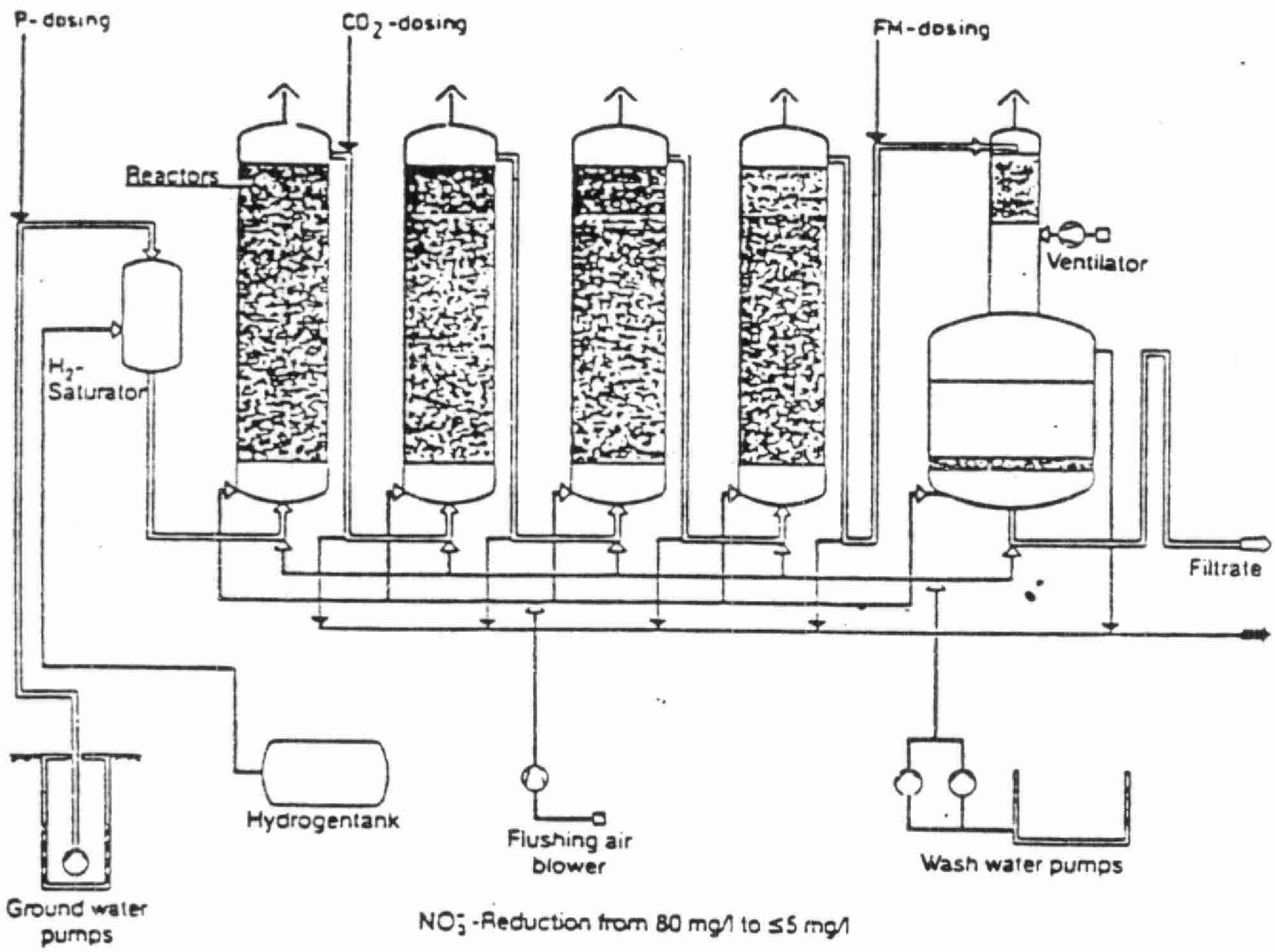
Water Treatment Work - Rasseln

Patent staus, if applicable:

EP 0 065 035 B1

Other information (e.g., funding source, cooperating agencies, etc.):

If available attach descriptive publications, technical literature, manufacturers' specifications, patent descriptions, etc.



Scheme of the Denitropur plant

Parameter		Ground-water	Effluent
Nitrat (NO_3)	mg/l	<75	<1
Nitrit (NO_2)	mg/l	<0,02	<0,01
Chlorid (CL)	mg/l	36	36
Total hardness	°d	11	11
Carbonate hardness	°d	<1	<4
pH Value		5,4	6;8

Industrial results of the Denitropur pla

Layout	
Flow rate m^3/h	50
Nitrate concentration raw water	80
(mg NO_3^-/l) denitrified water	<5
Nitrate elimination reaction rate (kg $N/m^3 \cdot d$)	0.25
Invest-cost	
Electro-mechanical part incl. erection	1.000
Laboratory equipment	110
Civil work	300
Div.	40
Total (1.000 DM)	1.450
Operating costs	
Capital costs (DM/m^3)	0.39
Operating costs (DM/m^3)	0.26
Total (DM/m^3)	0.65

Investment and operating costs of a Denitropur plant

Water and Waste-Water Engineering

SULZER

Treatment

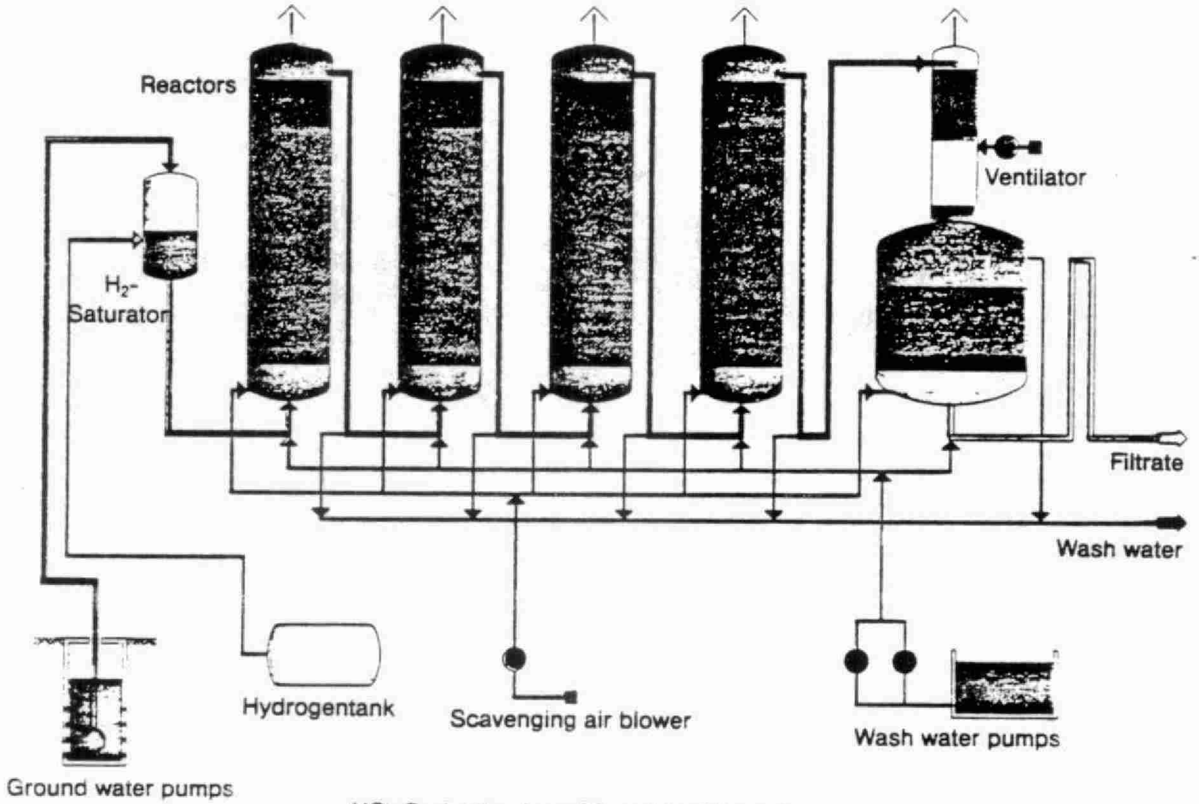
of

Nitrate-contaminated Drinking Water

DENITROPUR®-Process

WG-87

DENITROPUR®-INSTALLATION
MÖNCHENGLADBACH MUNICIPAL WATERWORKS



NO_3^--Reduction from 80 mg/l to ≤ 5 mg/l

Treatment of Nitrate-contaminated Drinking Water

1. Nitrates in drinking water

Over the past few decades, the nitrate content of numerous subterranean waters has increased considerably in the Federal Republic of Germany and in several other European countries.

The nitrate concentration (NO_3^-) in drinking water has to be kept low, due to the possibility of forming cancer-inducing nitrosamines after the reduction of nitrate to nitrite in the bowel and to the danger of causing cyanosis in small infants.

In accordance with the EEC Directives concerning Drinking Water Quality, the maximum permissible value for the nitrate content of drinking water is 50 mg/l and the standard value 25 mg/l.

The nitrate content of numerous subterranean and spring waters is determined by the condition of the ground, the nature of the vegetation or the agricultural exploitation of same: above all by the use (selection and extent) of fertilizers which has become current over the past few decades. Attempts to influence the situation, i.e. to lower the nitrate concentration in a particular subterranean water and the elimination of the practices causing the nitrate content to rise are long term in character. Hence many waterworks dealing with subterranean waters are nowadays compelled to use short or medium term process engineering measures to lower the nitrate content in a water intended for the drinking water supply network.

In some water supply undertakings it is possible to intermix subterranean waters containing nitrates with other waters whose nitrate content is very low. This is, however, not possible in some locations. Denitrification on site is then necessary.

2. Types of denitrification process

At present, the following processes can be applied for denitrification:

- Processes using ion exchangers
- Reverse osmosis
- biological denitrification.

- Processes using ion exchangers are characterized by a high consumption of chemicals. These chemicals are costly and result in concentrated solutions (effluent) which have to be suitably disposed of. Where the contaminant loading of the effluent is to be reduced, the ion exchanger plants have to be very complicated and expensive.
- Reverse osmosis uses higher pressures in order to separate the water from the ions dis-

solved in it via a semi-permeable membrane. Depending on the actual chemical content of the water, a preliminary and/or a final treatment stage are/is required also here. The disposal of the incident concentrates, i.e. the effluent, is here also a considerable problem.

- In the case of biological denitrification, there are two different processes, i.e. with heterotrophic and with autotrophic microorganisms.

- Heterotrophic denitrification processes have been tried out in various ways for the denitrification of drinking water. In this process, the residual amounts of organic substances, excess quantities of which may possibly have been metered in, e.g. methanol, ethanol or acetic acid, have to be broken down after completion of biological denitrification in order to be able to supply high quality drinking water.

- There has to be absolute certainty that no organic nutrient substrates penetrate into the drinking water supply network, since such a penetration would immediately lead to germ propagation.

3. Autotrophic dentrification using hydrogen

Autotrophic denitrification using hydrogen has a big advantage compared with a heterotrophic process, in that the use of hydrogen avoids problems associated with removing excess organic materials at the outlet of the plant.
In the course of this process, the nitrate is practically completely degraded and no salt or nitrate containing concentrates are produced. The residual is merely gaseous nitrogen.

The overall balance of the respiration sequence and energy generation by these so-called autotrophic microorganisms can be represented by the following equation:

$$5\,H_2 + 2\,H^+ + 2\,NO_3^- \rightarrow N_2 + 6\,H_2O$$

The oxygen atoms (O) of the nitrate (NO_3^-) serve to oxidize the hydrogen (H_2) to water (H_2O) and the nitrate is thus reduced to form gaseous nitrogen (N_2).
This reaction equation was confirmed experimentally.
Approximately 9 mg of H_2 are required to eliminate 100 mg NO_3^-.

The installation now operating at Mönchengladbach reduces the nitrate content of the subterranean water by about 80 mg/l NO_3^- to less than 5 mg/l NO_3^-, i.e. the decrease amounts to 93 %, and the design capacity is 50 m^3/h of raw water. The plant is very simple in layout and consists essentially of:

- hydrogen saturator
- Denitropur® reactors
- filter with aeration column.

The dimensions of the plant are such that it is capable of dealing with:

- 96 kg per day nitrate in the raw water and
- 6 kg per day in the filtrate.

Autotrophic denitrification occurs in the Denitropur® reactors, which are of fixed bed design. The carrier material used provides a large, well accessible surface for microorganism propagation. Good propagation and working conditions for the microorganisms result from the homogeneous distribution of all media. A sufficiently long retention time enables practically complete elimination of nitrates.
The necessary oxygen enrichment as well as the removal of the solid substances present in the subterranean water and produced as a result of denitrification take place in the final stage. This final stage, which is located downstream of the Denitropur® reactors, is made up of an oxidation column and a filter.
Suitable flushing units are employed for the backwashing of the Denitropur® reactors and of the filter.
Summarizing, the Denitropur® process provides the following advantages:

- Simple plant layout, hence high degree of operating reliability

- Admixing of only completely safe substances, which would not have any deleterious effect on the drinking water quality even should a faulty manipulation occur

- low chemical costs (hydrogen)

e.g. 80 mg NO_3^- = approx. 0.073 DM/m^3 water
50 mg NO_3^- = approx. 0.045 DM/m^3 water
30 mg NO_3^- = approx. 0.027 DM/m^3 water

- no loading of the waste water by salts, nitrates and other chemicals

Water and Wastewater Engineering
Sales program

Water engineering
Design and construction of complete installations and plant components for the treatment of spring-, ground- and surface-water to be used as drinking- or service-water for public and industrial utilities

Wastewater engineering
Design and construction of complete installations and plant components for the purification of industrial waste water for recycling, components recovery or discharge into the municipal sewage plants or the natural circuit, as well as for advanced treatment of municipal waste water

Sulzer Group
Activity program

Hot-water and steam generating plants
Components for nuclear power stations
Gas turbines
Diesel engines
Marine equipment
Water turbines
Storage pumps and pump-turbines
Valves and control systems for power stations
Syngas coolers
Pumps, compressors and blowers
Machinery for the fiber-cement industry
Plants for the manufacture of paper and millboard
Textile machines
Heating, ventilating and air conditioning systems
Plumbing and fire-protection systems
Refrigerating and cryogenic plants, heat pumps
Plants for distillation, evaporation and drying
Centrifuges and mixing processes
Water cooling systems
Irradiation plants
Medical engineering products
Locomotives and railcars
Electronic regulating and control devices
Industrial gears
Parts manufacture
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Biological Denitrification Process with Hydrogen-Oxidizing Bacteria for Drinking Water Treatment

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Introduction

The development of the DENITROPUR[R] process was started at the end of the 1970s. After considering all relevant methods, Sulzer decided on this particular one because it allows the most reliable biological treatment of a water supply to be achieved. The DENITROPUR process has properties which make its use in the preparation of drinking water very attractive:

- It is a biological process in which nitrate is selectively eliminated.
  Nitrogen gas is liberated during the process but no inorganic concentrates or salt solutions are produced;
- The substrate used (= nutrient for the microorganisms) is hydrogen which is completely harmless to potable water;
- In contrast to other substrates as methanol, ethanol or acetic acid etc., no further steps are needed to remove excess substrate;
- The conditions in the biological reactor are so selective, that only a few species of specific microorganisms can survive and develop;
- The reproduction rate (production of excess biomass) is desirably very low and only minimal amounts of biomass need to be disposed of;
- The technical side of the plant is extremely simple and robust. Process management is stable and reliable.

Laboratory and pilot studies, some of which were carried out under official supervision, have repeatedly confirmed the technical and economical feasibility of the process as well as the bacteriological cleanliness of the water produced.

The described plant has been supported by the German Federal Ministry for Research and Technology (BMFT) and has been realised at the treatment works of Rasseln, one of the different plants of the municipality of the town of Mönchengladbach (FRG).

After start-up in February 1986 the plant reached its full capacity and performance within some weeks. In the meantime the process results show that the Denitropur process is a very stable and reliable one. s,

After some basic considerations on the biological autotrophic denitrification with autotrophic hydrogen oxidizing microorganisms and on the basis of the process design, the Denitropur plant and the achieved results are described.

Hydrogen as Substrate for the Biological Denitrification

The use of hydrogen-oxidizing microorganisms for the biological denitrification has been described earlier (Bringmann and Kühn (1963), Schlegel (1976). It has been confirmed as a possible way for the drinking water production after different labor- and pilot-plant run, where the biological and chemical quality of the produced water was finally controled by the local water authority (Ginocchio (1980), Gros, Kyburz and Gmünder (1981-83), Berdat, Müller, Lienhart and Gros (1982).

The described nitrate elimination is carried out by autotrophic hydrogen oxydizing microorganisms which naturally occur in lakes, brooks or groundwater. These microorganisms are able to use molecular hydrogen as an electron donor. Through the oxidation of hydrogen, they are able to meet the energy requirement for assimilating inorganic carbon (CO_2, HCO_3^-). In the absence of oxygen, nitrate-ions are used as the source of oxygen and the nitrate becomes reduced to nitrogen. This reaction is called "dissimilatory nitrate reduction" or "nitrate respiration".

Only a few microorganisms are able to reduce nitrate in the presence of hydrogen. A strong biological selection thus occurs.

The reaction occuring in the process is represented by the equation:

$$5\ H_2 + 2\ H^+ + 2\ NO_3^- = N_2 + 6\ H_2O$$

which has been confirmed experimentally. In order to eliminate 100 mg NO_3^-, about 9 mg H_2 are needed. One can notice here the necessity to provide, beside molecular hydrogen, a given amount of hydrogen ions i.e. of acid. Part of it may be given by the buffering reaction of carbon dioxide present in the water to bicarbonate, the rest added in form of carbon dioxide or of anorganic acid. The amount of anorganic carbon necessary for the slow growth of the microorganism is easily covered by the anorganic carbon present in the water. If not present in sufficient amount in the water, nutrient (mainly phosphate) should be added too, mainly to cover cell growth. The reaction rate of the microorganisms and the completion of the reaction without nitrite formation is strongly dependent of the above mentioned parameter. Substrate and nutrient have to be made available at at least the stochiometric quantities and the pH-value, which plays a non-negligible role on the reaction rate (s. Kurt (1986), possibly kept at its optimum value.

The Basis of Process Design

The above mentioned conditions should be maintained for all active microorganisms in the biological reactor, i.e. through the whole depth of the biofilm.

The considered autotrophic microorganisms have a growth rate of the order of magnitude of 0.1 to 0.3 d^{-1}. As it is often the case in biological systems with such microorganisms, they must be kept or recycled within the system to avoid their "wash out".

Biological systems with fixed biomass are well adapted for such cases. There is no need for a possible sensitive separation stage where biomass would be separated from the produced water before being recirculated. Systems with attached biomass are thus well adapted for cases where the substances to be metabolized are present in small concentration and where relatively large variations of the operational parameters, f. ex. stop and go, are possible.

Different granular or filling materials may be used as carrier and operated either as fixed or as fluidized bed reactor.

In the present case the constraints to the carrier are many. First the concentration of microorganisms per unit volume of the system must be high as the reaction rate is relatively low. Second the reaction partners i.e. the nitrates in the raw water, the hydrogen and the microorganisms should be held in intensive contact with each other. Enough specific area of biofilm should thus be available per unit of volume and the energy input for mixing i.e. for mass transport of the substrates to the microorganisms used as efficiently as possible.

Mixing elements (Mellapak) from Sulzer with a 3-dimensional corrugated structure have been found in preliminary studies to be well suited carriers. In addition they perform an efficient fluid redistribution so that preferenced flow and dead zone may be avoided. Their operation and backwashing is very easy, as no expansion nor medium losses may occur. Furthermore they may have a large surface area which is readily available for colonisation by the microorganisms. A long enough residence time in the reactor was necessary to complete the nitrate elimination. The typical value ranged from 1 to 2 h. Increasing the pressure in the reactor leads to an increase (2 x) in the performance of the reactor. This can best be explained by the better transport mechanism of hydrogen to the biofilm and its deeper penetration, as the concentration of dissolved hydrogen is increased by pressure. Increasing the linear velocity of the recirculated water had a similar effect, which indicates here the importance and the way to influence the mass transport and the penetration of nitrate to the surface and in the depth of the biofilm.

All these considerations led to the design of the industrial plant (s. Fig. 1). The hydrogen is introduced before the reator system. The carriers are filled up in different reactors, designed in such a way that:

- The water is flowing through the reactors in series resulting in a concentration profile and in linear water velocities, which both enhance the reaction rate
- presure i.e. hydrogen concentration can be maintained high, at least at beginning of the reactor, where the nitrate concentration and the reaction rate reach their highest values
- efficient backwashing of the plant is possible while maintaining stable performances.

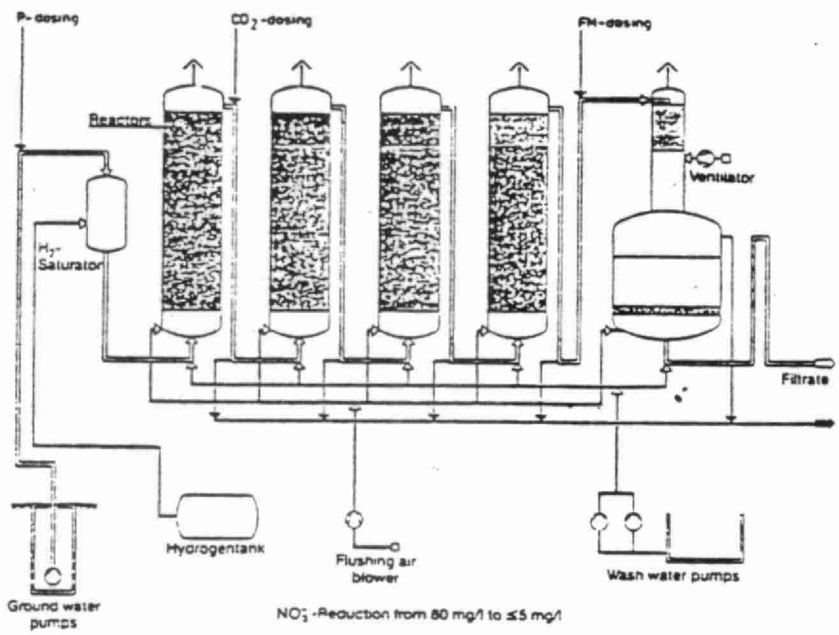

Fig. 1: Scheme of the Denitropur plant

The plant is laid out to treat ground water and produce 100 m³/h drinking water containing about 40 mg/l of nitrate. The available ground water containing about 80 mg/l of nitrate is denitrified in the DENITROPUR plant and then blended with untreated ground water. The nitrate load eliminated amounts to 90 kg NO_3/d. The process, as shown schematically on Fig. 1, consists of:

- ground water pumping station
- hydrogen inlet (saturation)
- PO_4 -dosing unit
- biological reactors containing the carrier
- Co_2-dosing unit
- counter current aeration
- two-layer filter
- UV-desinfection

The ground water is pumped with a pressure of 4 to 6 bar to the hydrogen inlet device, where it is saturated with hydrogen gas. The water flows then through the biological reactors connected in series.

There the dosage of acid and nutrient may be done at different positions of the system. After a certain number of reactors, i.e. after a certain residence time the water is completely denitrified and flows then over the counter current aeration, where it is oxygenated again and the excess of nitrogen and possibly of hydrogen is removed. After an addition of flocculating agent the water is filtered to eliminate possible small amounts of biomass and sterilized by U.V. The wash water produced in the plant is collected, cleared and percolated.

Fig. 2 is an outside view of the plant showing mainly the biological reactors. All the tubing, valves and control equipment are placed inside the building.

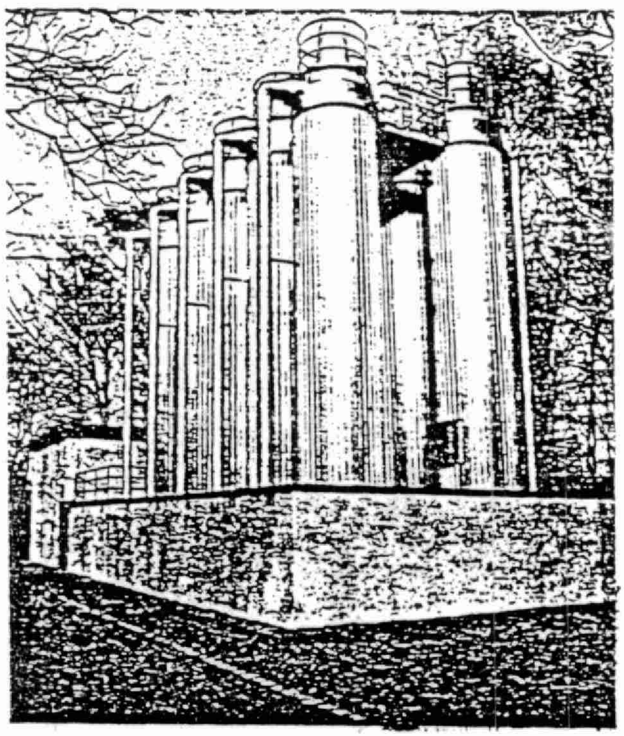

Fig. 2: Outside view of the Denitropur plant

Due to the hydraulic principle of the plant, the operation is straight forward and thus very stable and of easy operation and control, from the hydraulic as from the biological point of view.

From the view of the security authority it could be said that hydrogen, the main component of our old city-gas is much less critical than the earth gas present in every kitchen or the chlorine used in many water works. Nevertheless the concept of the plant includes a multiple active and passive safety such as:

- only in water dissolved hydrogen is present at very small concentrations in the biological reactors

- the room with the closed hydrogen inlet device is itself opened to the atmosphere and equipped with very sensitive hydrogen detectors
- no accumulation of gaseous hydrogen is possible in any part of the plant building.

Fig. 3 shows how the denitrifying performances still continued to grow until the nitrate could be eliminated to the specified level 5 mg NO_3/l within a residence time of the water in the reactor of about 1 hour.

The quality of the water reached after the biological reactor is represented on Tab. 1. The nitrate is eliminated to a very low value as it is the case for nitrite. Nitrite is always lower than 0.1 mg NO_2/l within the whole biological reactor and becomes lower than 0.01 mg NO_2/l when nitrate reaches the value of 1 mg NO_3/l.

Parameter		Ground-water	Effluent
Nitrat (NO_3)	mg/l	<75	<1
Nitrit (NO_2)	mg/l	<0,02	<0,01
Chlorid (CL)	mg/l	36	36
Total hardness	°d	11	11
Carbonate hardness	°d	<1	<4
pH Value		5,4	6;8

Table 1: Industrial results of the Denitropur plant

Beside a classical free programmable control unit for its "normal" operation of the plant, as it is a research object, is equipped with a lot of continuing measuring devices. This makes it possible to measure centrally parameters such as nitrate, nitrite, oxygen, hydrogen, pH, Redox, temperature and turbidity occuring at different locations in the plant and to store it for evaluation in an on-line computer.

The results presented in Table 1 were obtained after the plant had been optimized. It can be seen from these results that the aim of eliminating nitrate on a technical scale without a simultaneous formation of nitrite could be achieved. To express how the performance occurs during the process, Fig. 3 shows the concentration profile of Nitrate and Nitrite as a function of the residence time.

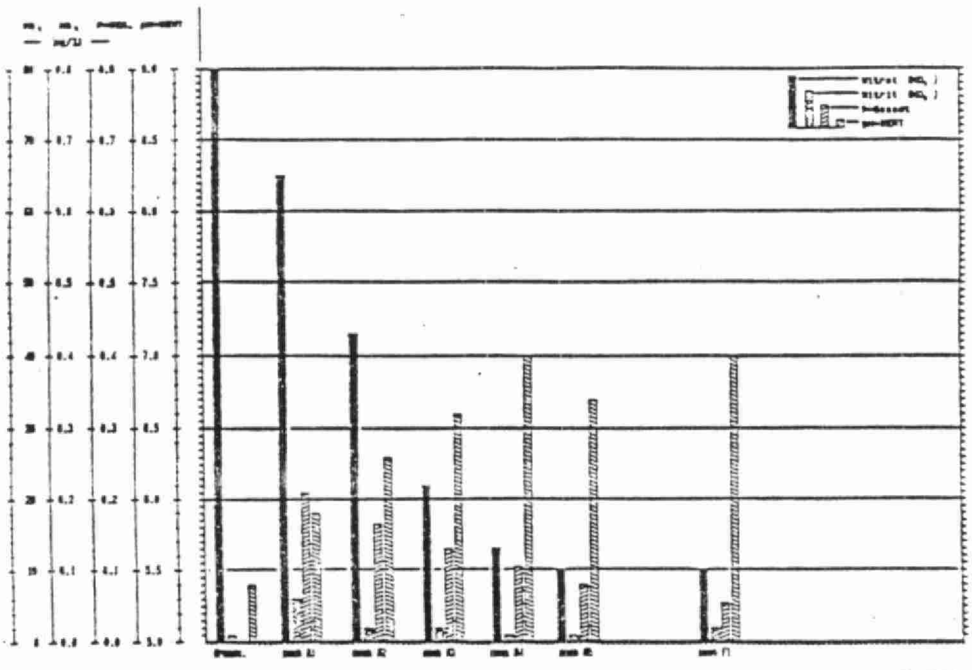

Fig. 3: Nitrate and nitrite concentration profile as a function of time

The results of the increase of the reaction rate of nitrate elimination with time confirm the order of magnitude of the growth rate of the autographic, hydrogen oxydizing microorganisms (growth rate - 0.1 to 0.3 d^{-1}). It follows that a single biological reactor unit will have to be washed about every 2 to 4 weeks to remove the excess biomass.

The fact that at the beginning of the line of biological reactors, the reaction rate of nitrate elimination has its highest value and then decreases. Although this fact could be explained by both higher concentration of nitrate and of hydrogen one gets there, the hydrogen concentration, if present in amounts superior or equal to stochiometry did not show a strong effect on reaction rate. This might be explained with the high molecular diffusion coefficient of hydrogen which deminishes resistance to mass transport to and within the biofilm.

This is less the case for the nitrate concentration and its influence on the reaction rate of nitrate elimination. Figures, which are found earlier by Gros and Ginocchio (1982), are quite confirmed and surpassed here. This strongly underlines the effect of mass transport primary to the biofilm and partly within the biofilm, both points which were considered carefully at the basis of the process design.

Further investigation, economical aspects

Beside the follow-up of the physico-chemical process parameter, which is realized by the municipal works of Mönchengladbach, the microbiology is followed by F. Selenka and R. Dressler from the Ruhr-Universität in Bochum. After having developed specific analytic methods and criteria to characterize the autotrophic cryophilic hydrogen oxydizing microoganisms, they already could follow the specific development of these autotrophic microorganisms. Although there are different microorganisms in presence, all belonging to the normal aquatic microflora, the autotrophic hydrogen oxydizing microorganisms have developed to population densities up to over 10^3 times more elevated than the other ones.

During the more than one year operation time of this first plant on technical scale the bacteriological and hygienic results have been in accordance to the regulations of the German drinking water standards (TVO)

Considering the economical aspect of the Denitropur-process it was found that the cost of the process using a plant of normal construction (not counting the numerous analytical and technical devices needed for the research program) and taking investment and operation costs into account amounts to 0,33 DM/m³ of drinking water. It has to be recognized that this figure has to be set in relation to the scale of the described plant.

Plants of larger scale will have less process cost.

It can thus be concluded that the Denitropur-process of nitrate removal by autotrophic hydrogen oxidizing microorganisms is fulfilling its performances and is competitive from the technical, microbiological and process aspect as well als from the economical one. (Table 2)

Layout		
Flow rate m^3/h		50
Nitrate concentration	raw water	80
(mg NO_3^-/l)	denitrified water	<5
Nitrate elimination reaction rate (kg $N/m^3 \cdot d$)		0.25
Invest-cost		
Electro-mechanical part incl. erection		1.000
Laboratory equipment		110
Civil work		300
Div.		40
Total (1.000 DM)		1.450
Operating costs		
Capital costs	(DM/m^3)	0.39
Operating costs	(DM/m^3)	0.26
Total	(DM/m^3)	0.55

Table 2: Investment and operating costs of a Denitropur plant